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RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

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[Continued from p. 383.]

PHOSPHO-VANADIO-MOLYBDATES.

Triple acids of this class are formed when solutions of phospho-vanadates are digested with molybdic teroxide; when vanadio-molybdates and alkaline phosphates are heated together in solution, especially in the presence of an acid; and when vanadic pent-oxide is heated with a solution of an alkaline phospho-molybdate.

The salts of this class are as a whole less stable than the vanadio-molybdates. They are, however, very well defined, and usually highly crystalline. In color they vary from an orange to a deep garnet, or ruby red. In general character they closely resemble the salts of the double compounds already described, and are often very beautiful.

Analytical Methods.—These are for the most part similar to those which I have already described. The three oxides may be precipitated together by mercurous nitrate and mercuric oxide, and then ignited with sodic tungstate in the manner described for the analysis of phospho-molybdates and arsenio-molybdates. The

[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

phosphoric oxide cannot be determined with accuracy by direct precipitation with magnesia-mixture. It is necessary first to remove the vanadic oxide. This may be done by dissolving the salt, adding ammonia in small but distinct excess, and afterward ammonic nitrate in large quantity. The solution is to be boiled for a short time, care being taken that after boiling free ammonia shall still be present. After standing in the cold for twenty-four hours the precipitated ammonic meta-vanadate may be filtered off, washed with a cold concentrated solution of ammonic nitrate, and titrated in the manner which I have described in speaking of the vanadio-molybdates. In the filtrate from the meta-vanadate phosphoric oxide may be determined by double precipitation with magnesia-mixture and final treatment with ammonic sulphide. Molybdic oxide is best determined by difference, the sum of the weights of the three oxides being known. Water, ammonia, and basic oxides may be found by the methods which I have already described in the cases of the binary compounds.

48 : 2 : 1 *Series.*—When 10 : 2 acid phospho-molybdate of ammonium, $10MoO_3.2P_2O_5.5(NH_4)_2O + 6Aq$, and ammonic meta-vanadate are dissolved together, there appears to be no reaction; but if a small excess of chlorhydric acid is added, and the solution is boiled, a beautiful deep orange-red crystalline precipitate is formed at once. This may be drained on a filter and washed with cold water, in which it is but slightly soluble. Hot water dissolves it rather more freely, but the salt cannot be purified by recrystallisation, as it is more or less completely decomposed by solution. Ammonia water dissolves it, forming a colorless liquid, in which baric acetate produces a nearly colorless precipitate. Of this salt,

1.3011 gram lost on ignition with WO_4Na_2 0.1399 gram = 10.75 per cent. $NH_3 + H_2O$.

1.0425 gram lost on ignition with WO_4Na_2 0.1124 gram = 10.78 per cent. $NH_3 + H_2O$.

1.5611 gram gave 0.1361 gram NH_4Cl = 4.24 per cent. $(NH_4)_2O$.

1.0113 gram gave 0.0900 gram NH_4Cl = 4.32 per cent. $(NH_4)_2O$.

1.3997 gram gave with MnO_4K 0.0304 gram V_2O_5 = 2.17 per cent.

{ 1.9173 gram gave with MnO_4K 0.0463 gram V_2O_5 = 2.41 per cent.
1.9173 gram gave 0.1112 gram $P_2O_7Mg_2$ = 3.71 per cent. P_2O_5.

In the last two analyses the vanadic pentoxide was first separated

by ammonic nitrate as VO_2NH_4; the phosphoric oxide was then determined in the filtrate.

The analyses correspond fairly well with the formula

$$48MoO_3.2P_2O_5.V_2O_5.7(NH_4)_2O + 30Aq.$$

		Calculated.	Mean.	Found.	
$48MoO_3$	6912	83.45	83.23	83.23(diff.)	
$2P_2O_5$	284	3.43	3.71	3.71	
V_2O_5	183	2.21	2.29	2.17	2.41
$7(NH_4)_2O$	364	4.39	4.28	4.32	4.24
$30H_2O$	540	6.52	6.50	6.50	6.51
	8283	100.00			

The compound may be regarded as a double salt, with the formula

$$2[16MoO_3.P_2O_5.2(NH_4)_2.H_2O] + 16MoO_3.V_2O_5.3(NH_4)_2O + 28Aq,$$

though, of course, other arrangements of the constituents are, in the present state of our knowledge, equally probable. Thus, we may also represent the results of the analyses by the expression,

$$2[12MoO_3.P_2O_5.2(NH_4)_2.H_2O] + 24MoO_3.V_2O_5.3(NH_4)_2O + 28Aq.$$

14 : 1 : 8 *Series.*—The beautiful yellow crystalline phospho-molybdates of ammonium, containing respectively twenty-four and twenty-two molecules of MoO_3 to one molecule of phosphoric oxide, slowly dissolve when boiled with a solution of ammonic meta-vanadate, giving a very fine deep orange-red liquid. After standing a few hours, the solution gives splendid deep ruby-red crystals in large quantity. These crystals appear to be octahedra; they dissolve readily in hot water to a deep orange-red liquid, without undergoing any apparent decomposition, and the salt crystallises from the solution unchanged. The solution gives no precipitate at first with baric chloride, but after a time very fine garnet-red crystals are formed in small quantity, mixed with a pale orange flocky or indistinctly crystalline substance, with an orange-red supernatant liquid. Potassic bromide in large excess gives an orange crystalline, and argentic nitrate a cinnamon-colored not distinctly crystalline precipitate. Mercurous nitrate and plumbic acetate gave orange precipitates. A solution of chloride of tri-

methyl-ammonium, $N(CH_3)_3HCl$, gives an orange precipitate in the concentrated solution, soluble in boiling water, and crystallising in beautiful small granular crystals, which are orange with an aurora-red tint. The crystals of the ruby-red salt became duller upon the surfaces when dried on woollen paper, but did not distinctly effloresce. Of this salt,

1.0686 gram lost on ignition with WO_4Na_2 0.2833 gram = 26.51 per cent. NH_3 and H_2O.

1.3051 gram gave 0.2245 gram NH_4Cl = 8.36 per cent. $(NH_4)_2O$.

1.1020 gram gave 0.3253 gram V_2O_5 = 29.51 per cent.

1.1113 gram gave 0.0598 gram $P_2O_7Mg_2$ = 3.44 per cent. P_2O_5.

The analyses lead to the formula,

$$14MoO_3.P_2O_5.8V_2O_5.8(NH_4)_2O + 50Aq.$$

		Calculated.		Found.	
$14MoO_3$	2016	40.83	73.36	40.54	73.49
$8V_2O_5$	1464	29.64		29.51	
P_2O_5	142	2.89		3.44	
$8(NH_4)_2O$	416	8.42		8.36	
$50H_2O$	900	18.22		18.14	
	4938	100.00			

If we assume that in this salt vanadic pentoxide stands in a relation to phosphoric oxide exactly analogous to that of molybdic teroxide, the compound will be of the same type as the phospho-molybdate already described,

$$22MoO_3.P_2O_5.xR_2O,$$

since we may write V_2O_5 as if its rational formula were $V_2O_2.O_3$.

In some preparations of this salt I observed the formation of two other salts in relatively small quantity. One of these formed pale orange-colored needles; the other, glimmering scales but slightly soluble in hot water.

PHOSPHO-VANADIO-TUNGSTATES.

These compounds bear a general resemblance to the phospho-vanadio-molybdates already described, and may be prepared by similar processes. They have usually a more or less deep orange or orange-red color, and very often exhibit a peculiar and highly

characteristic aurora-red tint. They are crystalline and well defined, and many salts of the different series are very beautiful.

Analytical Methods.—In all these salts it will, as in similar cases, be found most advantageous to determine the three acid-forming oxides by means of mercurous nitrate and mercuric oxide in the manner already pointed out. The estimation of phosphoric oxide may usually be made with a fair approximation to precision by direct precipitation with magnesia-mixture in the ammoniacal solution, redissolving the ammonio-magnesic phosphate, and precipitating a second time. In some cases I have found it better first to reduce the vanadic pentoxide to vanadic dioxide by boiling with strong chlorhydric acid, evaporating to dryness, and redissolving with the addition of a little tartaric and chlorhydric acids. A perfectly satisfactory method of estimating phosphoric oxide in these compounds remains to be discovered. Vanadic pentoxide may be estimated with accuracy by the methods already pointed out for the analysis of the vanadio-tungstates; that is, by boiling with strong chlorhydric acid, collecting the chlorine evolved in a solution of potassic iodide, and determining the free iodine by titration with sodic hyposulphite. A solution of potassic hypermanganate does not always oxidise vanadic dioxide in presence of tungstic, phosphoric, and free sulphuric acid, or only with great difficulty, so that the method is not generally applicable for the analysis of this class of compounds. Nitric acid, however, readily oxidises the dioxide under the same circumstances.

60 : 3 : 1 *Series.*—When the white insoluble phospho-tungstates of ammonium containing twenty-two or twenty-four molecules of tungstic to one of phosphoric oxide are dissolved in ammonia water, and a solution of ammonic meta-vanadate is added, no precipitate is formed; but if a small excess of chlorhydric acid is present in the boiling liquid, a fine lemon-yellow crystalline precipitate soon forms, which is to be well washed with a cold dilute solution of ammonic nitrate, as otherwise the salt passes readily through the filter, giving a milky liquid. The final washing may be made with a very dilute solution of the nitrate. After drying on woollen paper, the salt closely resembles tungstic oxide in color. It is almost insoluble in cold, and but slightly soluble in hot water, but with a large excess of ammonic phosphate it dissolves to a yellow solution; with ammonia water it gives a colorless solution. In a solution of ammonic carbonate it dissolves with strong efferves-

cence, indicating its distinctly acid character. The salt is not readily reduced by boiling with sulphuric and sulphurous acids, or by citric acid in the presence of chlorhydric acid, but easily by boiling with a strong solution of potassic cyanide, and, as is usual with this class of compounds, by fusion with the same salt.

Of this compound,

2.0684 grams lost on ignition with WO_4Na_2 0.2068 gram = 10.00 per cent. NH_3 and H_2O.

1.0971 gram gave 0.0747 gram NH_4Cl = 3.31 per cent. $(NH_4)_2O$.

1.3424 gram gave 0.0568 gram P_2O_7Mg = 2.71 per cent. P_2O_5.

2.5488 grams gave 0.1102 gram P_2O_7Mg = 2.77 per cent. P_2O_5.

1.0555 gram gave 0.0123 gram V_2O_5 = 1.16 per cent.

The analyses correspond very closely to the formula,

$$60WO_3.3P_2O_5.V_2O_5.10(NH_4)_2O + 60Aq,$$

which requires:

		Calculated.		Found.	
$60WO_3$	13920	86.29	90.00	86.10 (diff.)	90.00
$3P_2O_5$	426	2.64		2.71 — 2.77	
V_2O_5	183	1.15		1.16	
$10(NH_4)_2O$	520	3.23	9.92	3.31	10.00
$60H_2O$	1080	6.69		6.69	
	16129	100.00			

The compound is very probably a double salt, and may have the formula,

$$3[16WO_3.P_2O_5.3(NH_4)_2O] + 12WO_3.V_2O_5.(NH_4)_2O.2H_2O + 58Aq.$$

The arrangement of the constituents is here, of course, purely arbitrary, and must be regarded as only provisional. In the analyses above given the phosphoric oxide was determined directly and by double precipitation. The vanadic oxide was determined by boiling with chlorhydric acid and titration, in the manner already described.

16 : 1 : 3 *Series.*—A boiling solution of ammonic meta-vanadate dissolves the white insoluble phospho-tungstates of ammonium quite readily to a very deep orange-red solution. After standing some days, large deep orange or garnet-red crystals separate in quantity. They appear to be octahedra, and when first separated from the mother liquor are very beautiful; but on standing in the air they

lose their lustre, perhaps from a superficial effervescence, and become dull red. The salt is readily soluble in water, giving a deep orange-red solution, and crystallises from the solution unchanged. The constitution of this salt is represented by the formula,

$$16WO_3.3V_2O_5.P_2O_5.5(NH_4)_2O + 37Aq,$$

as the following analyses show:

1.0379 gram lost on ignition with WO_4Na_2 0.1826 gram = 17.59 per cent. NH_3 and H_2O.

1.2811 gram gave 0.1264 gram NH_4Cl = 4.80 per cent. $(NH_4)_2O$.

1.0652 gram gave 0.1074 gram V_2O_5 = 10.08 per cent.

1.0130 gram gave 0.0419 gram $P_2O_7Mg_2$ = 2.64 per cent. P_2O_5.

The formula given requires:

		Calculated.		Found.	
$16WO_3$	3712	69.67	82.62	69.69	82.41
$3V_2O_5$	548	10.28		10.08	
P_2O_5	142	2.67		2.64	
$5(NH_4)_2O$	260	4.88		4.80	
$37H_2O$	666	12.50		12.79	
	5328	100.00		100.00	

Adopting the provisional hypothesis which I have proposed above, that V_2O_5 as $V_2O_2.O_3$ may partially replace MoO_3 or WO_3 in these combinations, and that, on the other hand, V_2O_5 also replaces P_2O_5, we may write the formula given above,

$$8WO_3.2V_2O_2.O_3.P_2O_5.3(NH_4)_2O + 8WO_3.V_2O_5.2(NH_4)_2O.H_2O + 36Aq,$$

in which formula the first term is reduced to the type of

$$10WO_3.P_2O_5.3(NH_4)_2O.$$

The presence of five molecules of ammonic oxide shows that the salt belongs to the acid type so often met with in this class of compounds, and upon the view which I consider probable,[1] that the formulas of all the phospho-tungstates and phospho-molybdates as now received should be doubled, we should write the above formula

$$16WO_3.2V_2O_2.O_3.V_2O_5.P_2O_5.5(NH_4)_2O.H_2O + 36Aq;$$

corresponding to

$$16WO_3.2P_2O_5.5(NH_4)_2O.H_2O.$$

[1] Proceedings of the American Academy of Arts and Sciences, **17**, 89.

I consider this view of the subject as most probable in the present state of our knowledge.

60 : 3 : 2 *Series.*—When the 20 : 1 : 6 baric phospho-tungstate already described is boiled with vanadic hydrate, $VO(OH)_3$, the acid dissolves readily, and a beautiful orange-red solution is formed. On cooling, a salt separates in octahedral crystals, which have a very fine aurora-red color. The crystals dissolve rather easily in hot water, but are at the same time decomposed. A brownish orange salt then separates in distinct crystals, together with a white powder. The two can be separated mechanically. The mother liquor of the aurora-red salt yields on evaporation large dark-red crystals. Of the aurora-red salt,—

0.4165 gram lost on ignition with WO_4Na_2 0.0540 gram = 12.96 per cent.

1.1550 gram lost on ignition with WO_4Na_2 0.1500 gram = 12.98 per cent.

0.8819 gram gave of mixed oxides 0.6474 gram = 73.41 per cent.

1.4699 gram gave of mixed oxides 1.0784 gram = 73.37 per cent.

{ 1.5188 gram gave of mixed oxides 1.1145 gram = 73.38 per cent.
{ 1.5188 gram gave of $P_2O_7Mg_2$ 0.0508 gram = 2.14 per cent. P_2O_5

{ 1.0522 gram gave of mixed oxides 0.7709 gram = 73.26 per cent.
{ 1.0522 gram gave of $P_2O_7Mg_2$ 0.0380 gram = 2.31 per cent P_2O_5

1.3324 gram gave of V_2O_5 by titration 0.0258 gram = 1.93 per cent.

0.2693 gram gave of V_2O_5 by titration 0.0051 gram = 1.87 per cent.

The analyses correspond to the formula

$$60WO_3.3P_2O_5.2V_2O_5.18BaO + 144Aq,$$

which requires:

			Calculated.		Mean.				
$60WO_3$	13920	69.39		69.23		69.29	69.25	69.26	69.14
$3P_2O_5$	426	2.14	73.35	2.22	73.35	2.14	2.31		
$2V_2O_5$	366	1.82		1.90		1.93	1.87		
$18BaO$	2754	13.73		13.68		13.68			
$144H_2O$	2592	12.92		12.97		12.96	12.98		
	20058	100.00		100.00					

The baric oxide was determined by difference. In all determinations of the three acid oxides it was found necessary to ignite finally with a weighed quantity of normal sodic tungstate, in order

to expel the mercuric oxide completely, and obtain a constant weight. The aurora-red salt may be regarded as a double compound, with the possible formula

$$3[12WO_3.P_2O_5.4BaO.2H_2O] + 2[12WO_3.V_2O_5.3BaO.3H_2O] + 132Aq.$$

It has, I believe, the highest molecular weight, 20058, yet observed, though I shall describe a little farther on a phospho-vanadio-vanadico-tungstate with the formula

$$60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO + 150Aq,$$

with the molecular weight 20066. It will be interesting to determine the specific heats of bodies of this class, as well as the heat of formation. The formation of the aurora-red salt is very simply expressed by the equation,

$$3[20WO_3.P_2O_5.6BaO] + 2V_2O_5 = 60WO_3.3P_2O_5.2V_2O_5.18BaO,$$

the process being one of simple addition.

I have mentioned above the fact that a dark red salt crystallises from the mother liquor of the aurora-red salt. The following analytical results were obtained with the small quantity of this salt at my disposal:

0.7660 gram gave 0.5570 gram mixed oxides = 72.71 per cent.

1.0405 gram gave 0.2133 gram SO_4Ba = 13.45 per cent. BaO.

1.0405 gram lost on ignition 0.1451 gram = 13.94 per cent.

In the orange-brown salt formed by the decomposition of the aurora-red salt,

1.1919 gram lost on ignition with WO_4Na_2 0.1611 gram = 13.51 per cent.

1.0476 gram gave 0.7653 gram mixed oxides = 73.05 per cent.

1.4122 gram gave 0.3078 gram SO_4Ba = 14.31 per cent.

1.2372 gram gave 0.0087 gram V_2O_5 = 0.70 per cent.

No formulas can be deduced from these analyses, but they may serve to identify the salts analysed in future investigations.

18 : 3 : 4 *Series.*—The 24 : 1 phospho-tungstate of sodium already described, $24WO_3.P_2O_5.2Na_2O.4H_2O + 23Aq$, is readily dissolved by boiling with a solution of ammonic meta-vanadate, and gives a deep orange-red liquid. This solution does not yield crystals on evaporation, or after standing for some time. When, however, a solution of potassic bromide is added in large excess, a deep orange-red crystalline precipitate is quickly formed in large quantity. The

salt exhibits the peculiar aurora-red tint which is often observed when phosphoric acid or a soluble phosphate is mixed with a solution containing both tungstic and vanadic oxides. The compound dissolves in a rather large proportion of hot water, but at the same time undergoes decomposition, and the solution after a time deposits a bright orange-brown crystalline salt without the peculiar aurora-red tint. The first-mentioned potassic salt, as precipitated from a cold solution, allowed to stand twenty-four hours, then washed with cold water and dried on woollen paper, gave on analysis the formula

$$18WO_3.4V_2O_5.3P_2O_5.8K_2O + 32Aq,$$

which may perhaps be written

$$2[6WO_3.2V_2O_5.P_2O_5.3K_2O] + 6WO_3.P_2O_5.2K_2O.H_2O,$$

the type of the first compound being

$$8WO_3.P_2O_5.3K_2O.$$

1.1017 gram lost on ignition with WO_4Na_2 0.0973 gram = 8.83 per cent.

1.0803 gram gave 0.8646 gram mixed oxides = 80.03 per cent.

1.1159 gram gave 0.1218 gram V_2O_5 = 10.91 per cent.

1.2104 gram gave 0.1227 gram $P_2O_7Mg_2$ = 6.48 per cent.

The formula given requires:

		Calculated.		Found.	
$18WO_3$	4176	62.68	80.06	62.64	80.03
$4V_2O_5$	732	10.99		10.91	
$3P_2O_5$	426	6.39		6.48	
$8K_2O$	752	11.29		11.14	
$32H_2O$	576	8.65		8.83	
	6662	100.00			

7 : 1 : 1 *Series.*—The bright orange-brown salt formed by the decomposition of the 18 : 4 : 3 salt was in small distinct granular crystals. Of this salt,

0.9773 gram lost on ignition with WO_4Na_2 0.0780 gram = 7.98 per cent.

1.0160 gram gave 0.8205 gram mixed oxides = 80.76 per cent.

1.3077 gram gave 0.1037 gram V_2O_5 = 7.93 per cent.

1.0113 gram gave 0.0958 gram $P_2O_7Mg_2$ = 6.06 per cent. P_2O_5.

The analyses correspond, though not very closely, to the formula

$$7WO_3.V_2O_5.P_2O_5.3K_2O + 11Aq,$$

which requires:

		Calculated.		Found.	
$7WO_3$	1624	66.86	80.23	66.67	80.76
V_2O_5	183	7.53		7.93	
P_2O_5	142	5.84		6.06	
$3K_2O$	282	11.61		11.26	
$11H_2O$	198	8.16		7.98	
	2429	100.00			

According to the view which I have taken as to the function of V_2O_5 in this class of compounds, the 7 : 1 : 1 potassic salt belongs to the type

$$8WO_3.P_2O_5.3K_2O,$$

$V_2O_5.O_3$ taking the place of one molecule of WO_3. A much more extended study will be necessary to test this hypothesis. The vanadio-phospho-tungstates are probably numerous, and from their great beauty, as well as from their theoretic interest, form an attractive subject for investigation. The following notes may serve to furnish fresh points of departure: When the solution of vanadio-tungstate of sodium (obtained by boiling 12 : 5 acid sodic tungstate with the mixed oxides of vanadium and oxidising completely with bromine) is mixed with a solution of hydro-disodic phosphate, no apparent action takes place; but on boiling, the orange solution takes a deep red color, and soon deposits splendid ruby-red crystals in quantity. These crystals are decomposed in part even by cold water, which appears to separate phosphoric acid or sodic phosphate. An orange-colored sodium salt then separates. Almost exactly the same results are obtained when a solution of vanadio-tungstate of ammonium is boiled with a solution of ammonic phosphate. The liquid takes a beautiful deep red tint, and soon deposits splendid ruby-red crystals. The solution of the sodium salt, after a day or two, gives with one of trimethyl-ammonium chloride, $N(CH_3)_3HCl$, very fine granular ruby-red crystals. Of these crystals,

0.9752 gram gave 0.8549 gram mixed oxides = 87.66 per cent.

1.1543 gram gave 0.0631 gram V_2O_5 = 5.46 per cent.

1.0061 gram gave 0.0552 gram $P_2O_7Mg_2$ = 3.51 per cent.

The loss corresponding to water and trimethyl-ammonium oxide is 12.34 per cent. The ratio of the three oxides, WO_3, V_2O_5, and P_2O_5, is $34WO_3.3V_2O_5.2P_2O_5$; but the determination of the trimethyl ammonium oxide will be necessary in order to settle the formula completely. I am indebted to the kindness of Prof. Arthur Michael for a supply of the trimethylamin salt, which has proved of great service to me. The disposition of the corresponding oxide to form well-crystallised salts makes it a valuable test, and it should become an article of commerce for chemists' use.

VANADIO-VANADICO-MOLYBDATES.

The salt about to be described constitutes the type of a new and extensive series of complex acids, which contain two different linking oxides, embraced respectively under the formulas R_2O_5 and $R'O_2$, in which, however, R and R′ may be identical. The general formula for this class of molybdenum compounds may be written

$$m\mathrm{MoO_3}.n\mathrm{R_2O_5}.p\mathrm{R'O_2}.x\mathrm{R''_2O},$$

which, in the case of the identity of R and R′, becomes

$$m\mathrm{MoO_3}.n\mathrm{R_2O_5}.p\mathrm{RO_2}.x\mathrm{R''_2O}.$$

I shall show that there are corresponding salts containing tungsten in place of molybdenum. Vanadio-vanadico-molybdates are very readily formed by boiling a mixture of the two oxides of vanadium with an acid molybdate; by the partial reduction of vanadio-molybdates; or by digesting solutions of acid molybdates with solutions which contain vanadic dioxide and pentoxide.

28 : 4 : 1 *Vanadio-vanadico-molybdate of Ammonium.*—When pure ammonic divanadate is ignited in an open platinum vessel, and the remaining mass is boiled with an excess of a solution of 14 : 6 acid ammonic molybdate, a greenish solution is formed, which after filtration and evaporation yields on cooling a pale greenish-yellow crystalline salt. After draining on the filter-pump, the salt may be redissolved and recrystallised, when it presents very distinct granular greenish-yellow crystals. The solution is bright yellow. Of this salt,

1.4613 gram lost on ignition with WO_4Na_2 0.2527 gram = 17.29 per cent.

1.3326 gram gave by titration 0.1423 gram $(NH_4)_2O$ = 10.68 per cent.

1.2031 gram gave by titration 0.1288 gram $(NH_4)_2O$ = 10.71 per cent.

2.1968 grams gave 0.2184 gram V_2O_5 = 9.95 per cent. $VO_2 + V_2O_5$.

0.9980 gram gave 0.0607 gram VO_2 = 6.08 per cent. VO_2.

The analyses lead to the formula

$$28MoO_3.4V_2O_5.VO_2.11(NH_4)_2O + 20Aq,$$

which requires:

		Calculated.	Found.
$28MoO_3$	4032	73.56	73.34
$4VO_2$	334	6.09	6.08
V_2O_5	183	3.34	3.29
$11(NH_4)_2O$	572	10.44	10.68 10.71
$20H_2O$	360	6.57	6.60
	5481	100.00	

The compound is doubtless to be regarded as a double salt, but there are at present no data upon which to base even a conjectural arrangement. The salt is slightly soluble in cold water, the solution being strongly acid to litmus paper. It is soluble in hot water, and separates from the solution without sensible decomposition. The solution is reduced with great difficulty, either by sulphurous oxide or by sulphydric acid gas. For analysis I found it best, after oxidation with nitric acid, to boil with excess of ammonia, evaporate with ammonic chloride, and separate the ammonic meta-vanadate upon an asbestos filter. The vanadium was then determined by titration with hypermanganate. The vanadic dioxide was determined by hypermanganate in the solution of the salt, after adding phosphoric and sulphuric acids. It was found necessary to use very dilute solutions, and the close agreement of the determination of vanadic dioxide with the formula cannot be regarded as other than accidental. The reactions of this salt are as follows: the cold dilute solution gives no precipitate with salts of zinc, copper, manganese and cadmium; a pale yellow flocky precipitate with baric chloride, which soon becomes granular-crystalline; with potassic bromide, after some days, very fine, large prismatic crystals; with argentic nitrate, the solution gives a flocky precipitate, which is yellow with a tinge of buff; with mercurous nitrate, a bright, and with thallous nitrate, a pale yellow, flocky precipitate.

15 : 1 : 2 *Vanadio-vanadico-molybdate of Barium.*—Baric chloride added to the mother liquor from which the preceding salt was prepared gave a pale yellow crystalline, and, so far as could be seen, homogeneous precipitate in very small grains. This was filtered off, well washed with cold water, and dried on woollen paper for analysis. The filtrate was greenish, and gave no other salt on evaporation. The barium salt is very slightly soluble in cold water, and is decomposed by boiling water, with separation of baric molybdate, and formation of a pale greenish-yellow solution, which possibly contains a new salt of the same class. The salt is decomposed by boiling with mercurous nitrate, giving a bright yellow crystalline body. Boiled with argentic nitrate it gives an orange-colored precipitate which is also crystalline. Of this salt,

1.1690 gram gave 0.7260 gram $WO_3 + V_2O_5 + VO_2 = 62.09$ per cent. and 0.4772 gram $SO_4Ba = 26.80$ per cent. BaO.

1.5526 gram gave 0.6332 gram $SO_4Ba = 26.70$ per cent. BaO.

1.0341 gram lost on ignition 0.1127 gram = 10.90 per cent. H_2O.

2.1990 grams gave by titration 0.1748 gram = 7.95 per cent. V_2O_5

The titration was effected by $SO_4H_2 + SO_4(NH_4)_2 + 6Aq$ in a solution to which HCl had been added, after oxidation with nitric acid and addition of an excess of sodic carbonate. All the vanadium present was therefore estimated as V_2O_5.

The analyses correspond closely to the formula

$$30MoO_3.2V_2O_5.3VO_2.14BaO + 48Aq,$$

which requires:

		Calculated.	Found.	
$30MoO_3$	4320	54.40	54.40 (diff.)	
$2V_2O_5$	366	4.62	4.73	
$3VO_2$	249	3.13	3.22	
$14BaO$	2142	26.97	26.70	26.80
$48H_2O$	864	10.88	10.90	
	7941	100.00		

The compound is doubtless a double salt, and its formula may perhaps be

$$2[6MoO_3.V_2O_5.4BaO.2H_2O] + 3[6MoO_3.VO_2.2BaO.4H_2O] + 32Aq;$$

only it must be remarked that the empirical formula given above must be doubled in order to obtain a symmetrical structural formula, as the number of molecules of vanadic dioxide is uneven in the simpler expression given.

VANADIO-VANADICO-TUNGSTATES.

The class of salts to which I have given this name come also under the general formula

$$mRO_3.nR'_2O_5.pR''O_2.xR'''_2O,$$

and constitute, like the corresponding compounds containing molybdenum, a new ternary series. They are formed under the same conditions as these last, and like these have an orange or orange-red color, with a more or less distinct tinge of green.

12 : 2 : 3 (?) *Vanadio-vanadico-tungstate of Sodium.*—This salt, which was the first which I obtained containing vanadium, was formed by boiling with 12 : 5 acid sodic tungstate, a commercial vanadic pentoxide, which I owed to the kindness of Dr. J. Lawrence Smith, and which was probably prepared by igniting ammonic meta-vanadate, and therefore contained a certain proportion of vanadic dioxide. I did not succeed in preparing it a second time with a new preparation of the mixed oxides, and therefore trust that the incomplete analyses and meagre description of this and the corresponding ammonium and silver salts will be excused. The solution of the mixed oxides in the acid tungstate gave a deep orange-red solution, which, on evaporation to the consistency of a syrup, yielded after a time large orange-red apparently triclinic crystals, extremely soluble in water, and crystallising only from syrupy solutions. In this salt twice recrystallised,

0.5968 gram lost on ignition to fusion of the residue 0.1019 gram = 17.07 per cent.

0.6852 gram lost on ignition to fusion of the residue 0.1164 gram = 16.98 per cent.

0.3311 gram gave 0.2481 gram $WO_3 + V_2O_5 + VO_2 = 74.96$ per cent.

These analyses taken in connection with those of the ammonium and silver salts, may, with at least a certain degree of probability, be considered as leading to the formula

$$12WO_3.2V_2O_5.3VO_2.6Na_2O + 43Aq,$$

which requires:

		Calculated.	Found.	
$12WO_3$	2784			
$2V_2O_5$	366	74.79	74.96	
$3VO_2$	249			
$6Na_2O$	372	8.18	8.05	
$43H_2O$	774	17.03	16.99	17.07
	4545	100.00		

The solution of this salt had a deep orange-red color with distinct greenish reflections. Bromine water instantly gave a very fine deep orange solution, having nearly the color of potassic dichromate, and without the greenish tint: the liquid then contained only a sodic vanadio-tungstate. The solution gave flocky precipitates with various salts of heavy metallic oxides, and a bright red crystalline precipitate with argentic nitrate. A solution of acid potassic tungstate dissolved the mixture of oxides of vanadium, forming a greenish-orange solution, which also became bright orange-red with bromine. The potassic salt crystallised from this solution after evaporation to the consistency of a syrup, and gave crystals of peculiar greenish-orange tint. The solution of this salt gave a bright orange indistinctly crystalline precipitate with mercurous nitrate. This precipitate was decomposed by dilute chlorhydric acid, yielding a yellow solution from which no crystals were obtained by evaporation. This is perhaps the acid of the series.

12 : 2 : 3 (?) *Ammonium Salt.*—12 : 5 acid ammonic tungstate was boiled with a portion of the same commercial vanadic oxides in excess. The oxides dissolved readily, leaving, as in the cases of the sodium and potassium salts, a quantity of a black insoluble powder. The deep orange-yellow solution deposited on cooling beautiful orange-colored crystals of an ammonium salt; but on evaporating the main solution *in vacuo*, two kinds of crystals were obtained, one in relatively large dark-red octahedrons, the other much lighter-colored and resembling potassic dichromate. The darker salt gave in two analyses 17.98 and 18.05 per cent. of water and ammonic oxide. Of the lighter-colored salt separated mechanically from the first-named,

0.8429 gram lost on ignition 0.1149 gram = 13.63 per cent. H_2O and NH_3.

0.8164 gram lost on ignition 0.1107 gram = 13.56 per cent. H_2O and NH_3.

0.9047 gram gave 0.1502 gram NH_4Cl = 8.07 per cent. $(NH_4)_2O$.

The analyses agree, so far as they go, very well with the formula,

$$12WO_3.2V_2O_5.3VO_2.6(NH_4)_2O + 12Aq,$$

which requires:

		Calculated.	Found.
$12WO_3$	2784		
$2V_2O_5$	366	86.55	86.41 (diff.)
$3VO_2$	249		
$6(NH_4)_2O$	312	7.94	8.07
$12HO_2$	216	5.51	5.52
	3927	100.00	

The solution of this salt gives a beautiful scarlet precipitate with argentic nitrate, and a fine yellow precipitate with salts of strychnin, which after standing some hours becomes granular crystalline.

12 : 2 : 3 (?) *Vanadio-vanadico-tungstate of Silver.*—The salt analysed was in beautiful scarlet crystals, and was prepared by precipitating the ammonium salt with argentic nitrate, and washing with cold water. The salt is not distinctly crystalline when first thrown down, but becomes so after standing in the liquid. It is very slightly soluble in cold water, but dissolves in much hot water to a yellow liquid. Of this salt,

2.1193 grams lost on ignition 0.0621 gram = 2.93 per cent.

0.7511 gram gave 0.7420 gram AgCl = 28.21 per cent. Ag_2O.

These analyses agree with the formula,

$$12WO_3.2V_2O_5.3VO_2.6Ag_2O + 8Aq,$$

which requires:

		Calculated.	Found.
$12W_2O_3$	2784		
$2V_2O_5$	366	68.87	68.86 (diff.)
$3VO_2$	249		
$6Ag_2O$	1392	28.21	28.21
$8H_2O$	108	2.92	2.93
	4935	100.00	

The analyses which I have given may not be considered as sufficiently complete to establish the formulas assigned, but they serve to prove the existence of at least one class of vanadio-vanadico-tungstates. In substances of such high molecular weights the agree-

ment between the formulas of three different salts prepared under precisely the same conditions has a certain value, but it is less conclusive than when the molecular weight is lower, because such a change as is produced by writing, for instance, $2VO_2$ for V_2O_5, does not greatly affect the percentage results. If we admit the correctness of the formulas given, it will still be necessary to double them in order to construct a structural formula which shall be symmetrical, since the number of molecules of VO_2, either free or contained in V_2O_5, is uneven. For the complete analysis of compounds of this class it will be most advantageous to determine the vanadic pentoxide by heating with strong chlorhydric acid in the manner already indicated, and then to determine the dioxide in another portion by means of hypermanganate, if possible, or by first oxidising with bromine, and then determining the whole of the vanadium as pentoxide by boiling with chlorhydric acid and titrating as before.

PHOSPHO-VANADIO-VANADICO-TUNGSTATES.

I have given this rather ponderous appellation to a class of compounds in which vanadium exists partly as pentoxide and partly as dioxide. They may be regarded simply as double salts, but in the present state of our knowledge it will be found most convenient to consider them as a special class.

Salts of this type are formed whenever phospho-tungstates are mixed with vanadates in presence of vanadic dioxide, when vanadio-vanadico-tungstates are heated with solutions of alkaline phosphates or with phosphoric acid, and when phospho-vanadates and alkaline tungstates are brought together in presence of a reducing agent and of an acid. The salts are sometimes green and sometimes orange-red. In the last case they have frequently the peculiar aurora-red tint noticed among the colors of the phospho-vanadio-tungstates. They pass readily by oxidation with bromine or nitric acid into salts of the last-mentioned type, and they may be also derived from these by a partial reduction of the vanadic pentoxide.

Analytical Methods.—These are essentially the same as those which have been described. All the non-basic oxides may be determined together by means of mercurous nitrate and mercuric oxide, after complete oxidation with nitric acid. Phosphoric oxide may usually be determined directly, or after separation of a non-alkaline base, by double precipitation with magnesia mixture. The vanadic pentoxide can be estimated by boiling with chlorhydric

acid and titration in the manner already pointed out. To determine the vanadic dioxide the solution must first be oxidised completely, so as to convert the dioxide into pentoxide, any excess of the oxidising agent employed being carefully removed. I prefer to use bromine water for this purpose. The whole of the vanadium may then be determined by titration as above. The difference between the amount of vanadic pentoxide found before and after complete oxidation then gives, by a simple proportion, the corresponding amount of vanadic dioxide. It must be remembered that the sum of the non-basic oxides found by the mercury process requires to be corrected by adding the amount of oxygen required to convert the vanadic dioxide present into the equivalent of pentoxide. When the whole quantity of vanadium present is small, this correction may be neglected, as falling within the limits of the errors of analysis unavoidable with our present methods. Baric oxide in these salts is best estimated by difference, as the direct estimation almost always gives too high a percentage.

60 : 3 : 1 : 1 *Barium Salt.*—When ammonic vanadate is heated in a porcelain crucible until all the ammonia is expelled, the greenish residue consists, as already stated, chiefly of a mixture of vanadic dioxide and pentoxide. If this mixture be added in small portions at a time to a boiling solution of the baric phospho-tungstate, $20WO_3.P_2O_5.6BaO$, already described, the liquid takes at once a rather dull green color. The filtrate from the excess of mixed oxides, after evaporation in a water-bath and standing for some hours, yields a mass of deep green crystals, mechanically mixed with a relatively small proportion of a fine white powder, which may easily be removed by washing with cold water and pouring off the powder in suspension. The dark green crystals are regular octahedrons, frequently in long aggregates and beautifully defined. The salt is rather insoluble in cold but readily soluble in hot water, with a dark and rather dull green color. The cold solution, after adding dilute sulphuric acid, is not sensibly oxidised by potassic hypermanganate or in alkaline solution by iodine. The hot solution is oxidised by bromine and by nitric acid, and becomes deep orange-red. At a boiling heat potassic hypermanganate also oxidises it, the quantity required for oxidation being very small, so that it can with difficulty be estimated. Of this salt,

1.2596 gram gave 0.9178 gram mixed oxides = 72.86 per cent.

1.0160 gram lost on ignition 0.1362 gram = 13.40 per cent.

1.4649 gram lost on ignition 0.1969 gram = 13.44 per cent.
1.8580 gram gave 0.0624 gram $P_2O_7Mg_2$ = 2.15 per cent. P_2O_5.
1.3846 gram gave 0.0105 gram V_2O_5 = 0.76 per cent.
1.1972 gram gave 0.0131 gram V_2O_5 = 1.09 per cent.

In these analyses the vanadic pentoxide was determined directly in the salt, by boiling with chlorhydric acid and titrating. In two other analyses the vanadic dioxide was first completely oxidised by means of bromine; the whole quantity of vanadium was then determined as before. The percentage of vanadic dioxide was then calculated from the exces of V_2O_5 over that found by direct analysis. In this process,

1.1379 gram gave 0.0161 gram V_2O_5 = 1.44 per cent.
1.1714 gram gave 0.0200 gram V_2O_5 = 1.71 per cent.

The analyses correspond very closely to the formula,

$$60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO + 150Aq,$$

which requires:

		Calculated.	Found.	
$60WO_3$	13920	69.37	69.32	
$3P_2O_5$	426	2.12	2.15	
V_2O_5	183	0.92	1.09	0.76
VO_2	83	0.42	0.46	
18BaO	2754	13.72	13.72	
$150H_2O$	2700	13.45	13.40	13.44
	20066	100.00		

The baric oxide is estimated by difference. The relation of this salt to the aurora-red octahedral phospho-vanadio-tungstate of barium already described is interesting. We have respectively the formulas,

$$60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO + 150Aq,$$
$$60WO_3.3P_2O_5.V_2O_5.V_2O_5.18BaO + 144Aq,$$

and it is easy to see how, at least theoretically, one salt could be prepared from the other. With respect to the rational constitution of the green salt, it is possible at present only to form a provisional hypothesis. I am disposed to regard it as a triple compound, and to assign to it the formula,

$$3[12WO_3.P_2O_5.3BaO.3H_2O] + 12WO_3.V_2O_5.5BaO.H_2O + 12WO_3.VO_2.4BaO.$$

In this formula all the terms correspond to known compounds, the last to the dodeka-silico-tungstate type established by Marig-

nac, VO_2 replacing SiO_2. Of course, as in similar cases, various other formulas may be proposed. I lay no particular stress upon the view I have taken, which a wider and deeper study of these compounds may prove to be untenable. The formation of the salt may be expressed by the equation,

$$3[20WO_3.P_2O_5.6BaO] + V_2O_5 + VO_2 = 60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO.$$

The formula must be doubled to permit of a representation by means of a symmetrical structural formula. If we omit all the molecules of tungstic oxide except two, in order to save space, the linking portion of the structural formula of the corresponding acid may be written as follows:

$$\begin{array}{c}
\begin{array}{ccccc} & | & & | & \\ HO-WO_2 & - & - & - & WO_2-OH \end{array} \\
\begin{array}{ccccc} & | & & | & \\ & O & & O & \\ & | & & | & \\ & VO_2 & - & - & VO_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 2(HO)=VO-O-OV= & & & & (OH)_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 2(HO)=VO-O-OV= & & & & (OH)_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 2(HO)=PO-O-OP= & & & & (OH)_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 2(HO)=PO-O-OP= & & & & (OH)_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 2(HO)=PO-O-OP= & & & & (OH)_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 2(HO)=PO-O-OP= & & & & (OH)_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 2(HO)=PO-O-OP= & & & & (OH)_2 \end{array} \\
\begin{array}{ccccc} & | & & | & \\ 3(HO)\equiv PO-O-OP\equiv & & & & (OH)_3 \end{array}
\end{array}$$

This formula, which, like most of those which I have given, is purely conjectural, will at least serve to show how the two different states of oxidation of vanadium may be represented in the combination, and how the basicity of PO and VO may be affected by their position. Such formulas are not without value, as suggesting the possibility of forming new combinations, even if, as I prefer in this case to do, we consider the salt represented as double or triple. Structural formulas for double and still more for triple inorganic salts would probably be still more complex, and what I have aimed at is to show how all the valences may be satisfied in an arbitrarily selected compound containing four oxides of three different types.

The general results deducible from the formulas which I have given in the present instalment of my work are as follows:

1. Hypophosphorous and phosphorous acids may enter into combination with tungstic and molybdic oxides as links, so as to form complex inorganic acids. The structure of these four classes of acids indicates the possibility of forming new series of acids, in which methyl and other organic radicals or residues may take the place of the constitutional hydrogen of the hypophosphorous and phosphorous linking terms, and again of others in which, besides the replacement of hydrogen, phosphorus may be replaced by arsenic, and possibly by antimony and other elements.

2. Vanadium may replace phosphorus and arsenic so as to form well-defined series of vanadio-molybdates and vanadio-tungstates embraced under the general formula,

$$m\mathrm{RO_3}.n\mathrm{V_2O_5}.p\mathrm{R'_2O}.$$

3. Vanadic and phosphoric pentoxides may enter simultaneously into combination with tungstic or molybdic oxide, so as to form classes of triple acids embraced under the general formula,

$$m\mathrm{RO_3}.n\mathrm{P_2O_5}.p\mathrm{V_2O_5}.v\mathrm{H_2O}.$$

4. A class of quadruple acids exists into which, in addition to phosphoric and vanadic pentoxides, vanadic dioxide may enter, the general formula being

$$m\mathrm{RO_3}.n\mathrm{P_2O_5}.p\mathrm{V_2O_5}.r\mathrm{VO_2}.v\mathrm{H_2O}.$$

5. In another class of ternary or triple acids molybdic or tungstic oxide may be combined with both vanadic pentoxide and vanadic dioxide, the general formula being

$$m\mathrm{RO_3}.n\mathrm{V_2O_5}.p\mathrm{VO_2}.v\mathrm{H_2O}.$$

I shall show hereafter that all of these results are capable of further generalisation; that, for example, other oxides of the types $\mathrm{RO_2}$ corresponding to hydrates of the form $\mathrm{R(OH)_4}$ may replace $\mathrm{VO_2}$ or $\mathrm{V(OH)_4}$; that other pentoxides may replace $\mathrm{P_2O_5}$, $\mathrm{As_2O_5}$, and $\mathrm{V_2O_5}$, either in the presence or in the absence of oxides of the type $\mathrm{RO_2}$; in short, that the complex inorganic acids form a new department of inorganic chemistry, and not a series of isolated compounds.

(*To be continued.*)

EXPERIMENTS ON THE ESTIMATION OF LEAD AS LEAD DIOXIDE BY MEANS OF THE ELECTRIC CURRENT.

By Frank Tenney.

These experiments were undertaken to investigate anew the practicability of the determination of lead as lead dioxide in acid solution. The first experiments in this direction were made by Luckow[1] and by May.[2] May used a solution containing copper and 2½ per cent. of free nitric acid (calculated as anhydrous HNO_3), and obtained in this solution satisfactory results, weighing the lead as lead monoxide, into which the dioxide was converted by heat. Luckow[3] says: "The complete precipitation of the lead occurs only in the presence of at least 10 per cent. of free nitric acid, if only lead be present. If the solution contain copper also, less free acid is required. With less than 8 per cent. free nitric acid, lead is liable to be thrown down on the negative pole with the copper as metal."

Riche[4] proceeds in the same way as Luckow, but warms the solution to 60°–90°. The work of Parodi and Mascazzini[5] in solutions containing tartrates, and of Classen and von Reis[6] in oxalate solutions, relates to the precipitation of metallic lead, and has therefore little connection with the present subject.

The substance used for analysis in the present experiments was lead nitrate, whose purity was proved by estimating the lead. This was done by igniting the lead nitrate and weighing the residual oxide, PbO.

Two determinations gave:

	I.	II.	Theory requires.
Weight PbN_2O_6 taken	0.8005	0.9713	
Weight PbO found	0.5395	0.6542	
Per cent. of Pb	62.54	62.54	62.54

A solution was made of this lead nitrate containing 1.4690 gram to the litre, and 25 cc. of this solution were taken each time for analysis. Of this solution, 25 cc. should yield 0.0266 gram dioxide.

[1] Zeitschrift für analytische Chemie, **11** (1872), 9-12; **19** (1880), 1.
[2] American Journal of Science, [3] **6**, 255. [3] Zeitschrift für analytische Chemie, **19**, 15.
[4] Annales de Chimie et de Physique, [5] **13**, 508.
[5] Zeitschrift für analytische Chemie, **18**, 588.
[6] Berichte der deutschen chemischen Gesellschaft, **14**, 1622.

In a neutral solution the lead was deposited partly as metallic lead on the negative, and partly as lead dioxide on the positive electrode. Three portions of the solution were then taken, and to No. I 1½ per cent. of free nitric acid (calculated as anhydrous HNO_3), to No. II 5 per cent., and to No. III 10 per cent. were added. After 16 hours' action of the current the amount of lead dioxide thrown down was found to be:

I.	II.	III.	Calculated.
0.0216	0.0253	0.0265	0.0266

The coating on No. I was not strongly adherent.

In the next trial, No. I received 10 per cent., No. II 13⅓ per cent., No. III 16⅔ per cent. of free nitric acid; the results were:

I.	II.	III.	Calculated.
0.0266	0.0274	0.0272	0.0262

In the next trial 50 cc. solution of lead nitrate were taken and 10 per cent. of free acid added. The results were:

I.	II.	III.	Calculated.
0.0533	0.0533	0.0452	0.0532

In No. III, owing to irregularity of the current, the dioxide came down unequally and scaled off badly.

A solution of copper containing 0.2920 gram copper in 25 cc. was made up, and three portions, each containing 25 cc. of this solution and 25 cc. of the lead solution, were subjected to the action of the current after adding to No. I 1½ per cent., to No. II 5 per cent., and to No. III 10 per cent. of free nitric acid. The results were:

I.		II.		III.		Calculated.	
PbO_2.	Cu.	PbO_2.	Cu.	PbO_2.	Cu.	PbO_2.	Cu.
0.0278	0.2967	0.0281	0.2924	0.0275	0.2930	0.0266	0.2920

The copper was in all cases slightly black.

In presence of iron with 1½ per cent., 5 per cent. and 10 per cent. of free acid the results were:

	I.	II.	III.	Calculated.
PbO_2	0.0261	0.0259	0.0200	0.0266

The last one scaled off badly, thus accounting for the low result. The electrodes used had areas of 73.13, 75.19 and 66.49 square centimeters respectively.

To sum up, one may say this method is reliable where the amount of lead is not too large and where there is a sufficient

amount of free nitric acid present. Where the lead does not exceed 0.02 gram it may be thrown down as lead dioxide and weighed on ordinary flat electrodes. Where larger amounts are present, aliquot parts of a solution must be taken, or a platinum dish may be made the positive pole and the dioxide washed by decantation.

Since these experiments were made this method has been largely used in this laboratory for the estimation of lead in galena and in slags and mattes. From 10 per cent. to 20 per cent. of free nitric acid should be present; if there is too much, the lead dioxide, as fast as it is thrown down, redissolves in the nitrous acid resulting from the decomposition of the strong nitric acid. In slags and mattes the most satisfactory method is found to be as follows: After decomposition in the usual way, the lead and copper are precipitated as sulphides with sulphuretted hydrogen, these sulphides are dissolved in nitric acid, and the solution put in the circuit. A perfect and complete separation of the lead and copper is obtained. The small amount of sulphuric acid formed by the solution of the sulphides in nitric acid does not affect the accuracy of the determination.

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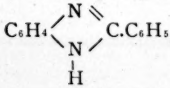
A NITRILE OF ANHYDRO-BENZDIAMIDO-BENZENE.

By Jas. Lewis Howe.

When the so called anhydro-benzdiamido-benzene of Hübner,[1] (Benzenyl-phenylene-amidine of Beilstein[2]) of the formula



$C_6H_4 \begin{cases} N \\ \diagdown \\ \diagup \\ N \\ | \\ H \end{cases} C.C_6H_5$, is heated in a closed tube with an excess of cyanogen iodide, CNI, and a considerable quantity of benzene, a reaction takes place slowly at slightly below 100° C., and the tube becomes

[1] Annalen der Chemie, **208**, 302. [2] Beilstein, Handbuch der Organischen Chemie, 2049.

lined with dark red crystals of the triiodide of the anhydro-base, $C_6H_4\begin{matrix}N\\ \diagup\\ \diagdown\\ N\end{matrix}\!\!>\!C.C_6H_5I_2$, while the benzene leaves upon evaporation a dark crystalline mass. This is for the most part soluble in hot petroleum ether (of boiling point 60°–70° C.), out of which it crystallises in small, lustrous, lemon-yellow tables, approximately hexagonal in shape. These melt at 105.5° C. (corrected), and analysis shows them to have the formula $C_{13}H_9N_2CN$, showing that a hydrogen atom of the anhydro-base has been replaced by the group CN. The analyses are as follows:

I. 0.1880 gram gave 0.5277 gram CO_2 and 0.073 gram H_2O.

II. 0.2488 gram gave 0.7041 gram CO_2 and 0.111 gram H_2O.

III. 0.28 gram gave 0.7845 gram CO_2 and 0.1155 gram H_2O.

IV. 0.1643 gram gave at 9° C. and 768 mm. pressure 26 ccm. = 0.0316 gram N.

V. 0.1965 gram gave at 17.5° C. and 771 mm. pressure 32 ccm. = 0.0376 gram N.

VI. 0.15 gram gave at 5° C. and 768 mm. pressure 23 5 ccm. = 0.029 gram N.

	Calculated for $C_{14}H_9N_3$.	Found. I & V.	II & IV.	III & VI.
C	76.71	76.55	77.17	76.41
H	4.11	4.31	4.46	4.58
N	19.18	19.13	19.24	19.37

This nitrile is very stable, not decomposing at a very high temperature; it distils slowly with steam, and may in this way be obtained in a pure state, showing scarcely a trace of yellow color. It is easily soluble in alcohol, cold benzene, and hot petroleum ether; very slightly soluble in cold petroleum ether, and insoluble in water; in chloroform, glacial acetic acid and acetone it is exceedingly soluble. It crystallises out of benzene and alcohol in large needles; no crystals could be obtained from any of the above solutions suitable for crystallographical investigation.

In order to determine if possible which hydrogen atom was replaced by the CN group, I endeavored to change this group into the carboxyl; but in this I did not succeed.

By boiling the nitrile in a solution of caustic potash in water it was dissolved, ammonia given off, and from the solution a white

precipitate was thrown down by hydrochloric acid, which dissolved in excess of the acid, and was again precipitated by ammonia. This precipitate was found to be the original anhydro-base, and the reaction may have been

$$C_{13}H_9N_3CN + KOH + HOH = NH_3 + C_{13}H_9N_2COOK,$$

followed immediately by the decomposition,

$$C_{13}H_9N_3COOK + KOH = K_2CO_3 + C_{12}H_{10}N_2;$$

or, possibly,

$$C_{13}H_9N_3CN + KOH = C_{12}H_9N_2H + CONK,$$

and $$CONK + KOH + HOH = K_2CO_3 + NH_3.$$

In a second case the nitrile was gradually heated with water in a closed tube to 250° C. The greater part remained unchanged, but a small portion was decomposed into the original anhydro base, and the odor of the ammonia formed could be detected.

Claisen's method was also tried; but this was also unsuccessful. Hydrochloric acid gas was led into concentrated hydrochloric acid, which was kept in a freezing mixture until the acid became as concentrated as possible. In this a portion of the nitrile was placed, and allowed to remain twenty-four hours at a temperature considerably below 0° C. The nitrile dissolved very gradually; but from the solution only the hydrochloric acid salt of the anhydro base was obtained.

I further attempted to convert the CN group into the methyleneamine group, CH_2NH_2, by the use of sodium amalgam and water. In this case also the CN group was removed and the anhydro base alone obtained. It would, therefore, seem that the CN group replaces the hydrogen of the imine group. Were this not the case we should expect the formation of isomers; but there was in the tubes after heating no trace of any compound derived from the anhydro-base, except the nitrile and the triiodide. Further, were the CN group connected directly with a carbon atom of either o the benzene radicals, it would in all probability give an acid and an amine. On the contrary, the CN seemed to be easily separated from the rest of the molecule, as we should expect in case it were attached to a nitrogen atom. Hence, the probable formula of the nitrile is $C_6H_4 \begin{cases} N \\ \diagdown\!\!\diagup \\ N \end{cases} C.C_6H_5$, and its formation is expressed thus,

$C_{13}H_{10}N_2 + ICN = C_{14}H_9N_3 + HI$. A part of the hydriodic acid forms a salt of the anhydro-base, and the rest is decomposed into hydrogen and iodine, the latter uniting with the above salt to form a triiodide,

$$4C_{13}H_{10}N_2 + 3ICN = 3C_{14}H_9N_3 + C_{13}H_{11}N_2I_3 + H_2.$$

This compound is thus probably a cyanamide—anhydro-benzdiamido-benzene cyanamide—but, unlike most of these, it shows no tendency to polymerise. I shall hope soon to be able to make and study one or more of the isomers of this compound, in which the CN group shall be attached to one of the benzene radicals.

Brooks Laboratory, Cleveland, O., *May*, 1883.

THE ETHYL DERIVATIVES OF ANHYDRO-BENZDIAMIDO-BENZENE.

By Jas. Lewis Howe.

For some years past the action of various alkyl iodides upon the so-called anhydro-bases of Hübner has been studied in the chemical laboratory at Göttingen.[1] The base which has been most studied is anhydro-benzdiamido-benzene, the benzenyl-phenylene-amidine of Beilstein;[2] of the formula $C_6H_4<\begin{matrix}N\\ \diagdown\\ N\\ \diagup\\ H\end{matrix}>C.C_6H_5$. When this is heated for several hours in a closed tube with an alkyl iodide at a temperature from 150° to 260° C., a dialkyl triiodide is generally formed of the formula $R''N(C_xH_y)_2I_3$, and this by treatment with lead hydroxide and afterward with potassium hydroxide, gives a hydroxide, $R''N(C_xH_y)_2OH$, which possesses more strongly basic properties than the anhydro-base. In a few instances where the heat used was rather low, the hydriodic acid salt of a monoalkyl base, $R''N.C_xH_y.HI$, has been formed; but the formation of this monoalkyl base seems to be, however, rather the result of chance than of any definite conditions. Hence it seemed desirable to study these relations more closely, and this paper is a resumé of the results obtained with ethyl iodide.

[1] Annalen der Chemie, **210**, 328. [2] Beilstein: Handbuch der Organischen Chemie, 2049.

Finely powdered anhydro-benzdiamido-benzene in quantities of about five grams was heated with an excess of ethyl iodide in a closed tube, at the lowest temperature at which a complete reaction took place. No pressure was noticed upon opening. When heated for twenty-four hours at 120° C. the tube contained for the most part straw-colored crystals, there being present but small quantities of the dark red crystals of the triiodides. The straw-colored crystals were found to consist of approximately equal parts of the iodide of the diethyl derivative and the hydriodic acid salt of the anhydro-base. No trace of a monoethyl derivative was in any instance to be detected.

The separation of the above salts by crystallisation is very difficult, but the bases may be easily separated by treating the aqueous solution of the iodides with soda, which precipitates completely the anhydro-base. After boiling, this is easily filtered off, and the diethyl hydroxide is precipitated by caustic potassa, its salts being decomposed only by the caustic alkalies. The following is a description of the base and several of its salts.[1]

Diethyl-anhydro-benzdiamido-benzene hydroxide (*Benzenyl-diethyl-phenylene-amidine of Beilstein*).—Melting point, 136° C. (corrected); crystallises in colorless monoclinic prisms, consisting of the faces ∞P and oP. The angle of the principal axis is very much inclined, but owing to the oP face being in no case smooth, it was impossible to determine the angle accurately. The crystals were also too brittle for optical investigation. It is insoluble in water and the alkalies, difficultly soluble in petroleum ether, easily in cold alcohol, ether, and acetone, and especially soluble in benzene and chloroform. It dissolves readily in dilute acids, forming salts, and from the solution of these it is reprecipitated by caustic alkalies.

Analyses:

I. 0.3260 gram gave 0.9175 gram CO_2 and 0.2293 gram H_2O.
II. 0.3370 gram gave 0.9464 gram CO_2 and 0.2423 gram H_2O.
III. 0.2286 gram gave 0.0235 gram N.
IV. 0.1792 gram gave 0.01845 gram N.

[1] This diethyl base and its salts have been formed by Simon and Pichler (cf. Annalen der Chemie **210**, 360) by heating the anhydro-base with ethyl iodide at 260°, giving the triiodide, which is decomposed by $Pb(OH)_2$ and KOH. As there were some marked differences, I used also this method of forming the base, and am led to the conclusion that the base formed from the triiodide is identical with that from the monoiodide. The former base as described melted at 132° C., was very soluble in petroleum ether; the iodide contained no water of crystallisation, and the chloride differed very materially. These seem to be errors of observation, caused by an insufficiency of material.

Calculated for $C_6H_4\langle{}^{N}_{N}\rangle C.C_6H_5$.
$(C_2H_5)_2OH$

		Found.	
		I & III.	II & IV.
C	76.12	76.75	76.59
H	7.46	7.84	7.98
N	10.45	10.30	10.29
O	5.97		

Diethyl-anhydro-benzdiamido-benzene iodide, $C_{13}H_9N_2 : (C_2H_5)_2I$, H_2O.—Crystallises rapidly out of a hot concentrated aqueous solution in fine colorless needles; if the solution is less concentrated the crystallisation is slow, and prisms, sometimes long and slender, sometimes short and thick, and pale straw color, are formed. It is easily soluble in hot water, rather difficultly in cold; the solution is very slowly decomposed by long standing, iodine being liberated; the crystals become opaque upon heating.

Analysis:

I. 0.1612 gram gave 0.0952 gram AgI.
II. 0.1581 gram gave 0.0939 gram AgI.
III. 0.2786 gram gave 0.1608 gram AgI.
IV. 0.2314 gram lost at 135° C. 0.0110 gram H_2O.
V. 0.3113 gram lost at 140° C. 0.0140 gram H_2O.

Calculated for $C_{13}H_9N_2 : (C_2H_5)_2I, H_2O$.

		Found.		
		I & IV.	II & V.	III.
I	31.98	31.92	32.06	31.80
H_2O	4.55	4.75	4.50	

Diethyl-anhydro-benzdiamido-benzene chloride, $C_{13}H_9N_2 : (C_2H_5)_2Cl$, $2H_2O$.—Formed by dissolving the hydroxide in hydrochloric acid, neutralising the solution with soda, evaporating to dryness, and extracting with absolute alcohol. It crystallises from a concentrated neutral solution in colorless tables, which remain unchanged in the air, and are easily soluble in water. It loses its water of crystallisation over sulphuric acid or at 100° C. The neutral solution of the chloride decomposes slowly by standing.

Analysis:

0.2694 gram lost at 100° C. 0.0301 gram H_2O and gave 0.12 gram AgCl.

Calculated for $C_{13}H_9N_2 : (C_2H_5)_2Cl, 2H_2O$.		Found.
Cl	11.01	11.01
H_2O	11.18	11.18

A second chloride crystallises imperfectly out of a very concentrated acid solution, with one molecule of hydrochloric acid and several molecules of water. By long standing over sulphuric acid or by heating, the water is given off molecule by molecule; at 130° C. the salt contains two molecules of water, which it loses below 165° C., and at the same time a molecule of hydrochloric acid is given off, leaving the anhydrous monochloride above described.

Double platinum chloride, $[C_{13}H_9N_2 : (C_2H_5)_2Cl]_2PtCl_4$.—Precipitated from a solution of the chloride by platinic chloride in very fine orange crystals; from a hot solution the crystals are sometimes quite large.

Analysis:

I. 0.1994 gram gave 0.0433 gram Pt.

II. 0.2073 gram gave 0.0446 gram Pt.

		Found.	
Calculated for $[C_{13}H_9N_2 : (C_2H_5)_2Cl]_2PtCl_4$.		I.	II.
Pt	21.60	21.71	21.51

Diethyl-anhydro-benzdiamido-benzene sulphate, $C_{13}H_9N_2 : (C_2H_5)_2O.SO_2.OH,H_2O$.—Crystallises out of a concentrated aqueous solution in large flat colorless crystals. It loses its water of crystallisation very rapidly over sulphuric acid, but not over calcium chloride.

Analyses:

I. 0.1828 gram gave 0.1190 gram $BaSO_4$.

II. 0.4276 gram lost 0.02105 gram H_2O and gave 0.2720 gram $BaSO_4$.

III. 0.1528 gram lost 0.0076 gram H_2O.

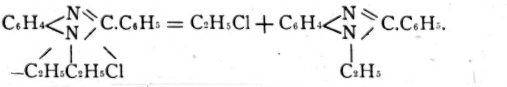
IV. 0.1328 gram lost 0.0065 gram H_2O.

V. 0.4707 gram lost 0.0231 gram H_2O.

		Found			
Calculated for $C_{13}H_9N_2 : (C_2H_5)_2SO_4H,H_2O$.		I & III.	II.	IV.	V.
H_2O	4.92	4.92	4.92	4.88	4.91
S	8.74	8.92	8.74		

Ethyl-anhydro-benzdiamido-benzene.—When the chloride is heated to a temperature above 200° C. it gradually decomposes, giving off a gas resembling in odor ethylchloride, and a thick oil distils over. This oil may be purified by dissolving in acids and reprecipitating with ammonia. It is extremely soluble in all solvents, except water and petroleum ether, being in these but slightly

soluble; after the evaporation of the solvent it remains as an oil; but by gently warming, to drive away the last traces of the solvent, and then allowing it to stand several hours, it becomes gradually crystalline. Analysis proved that this compound is monoethyl-anhydro-benzdiamido-benzene. It melts at 80°–81° C. and possesses basic properties, not, however, as strong as those of the corresponding diethyl base. The reaction for the formation of this base is the following:



This process could undoubtedly be applied to similar dialkyl anhydro-bases, as a definite method of forming the monoalkyl compounds, which have hitherto been the result of no known conditions. It is worthy of note that the salts of the monoethyl base are very unstable, being decomposed by boiling with even dilute acids, forming the corresponding salt of the anhydro-base. The corresponding salts of the diethyl base are comparatively stable, being unaffected even by strong acids, and only decomposed at quite high temperatures. The salts of the diethyl base are much more soluble in water than those of the monoethyl base; the monoethyl base, however, is itself somewhat soluble in water, while the diethyl base is insoluble. The following are analyses of the monoethyl base and its salts:

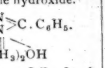
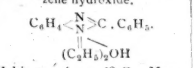
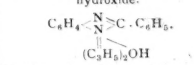
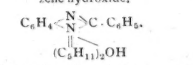
Ethyl-anhydro-benzdiamido-benzene, $C_{13}H_9N_2.C_2H_5$.

I. 0.1405 gram gave 0.4158 gram CO_2 and 0.0872 gram H_2O.
II. 0.1361 gram gave 0.0172 gram N.
III. 0.1354 gram gave 0.0170 gram N.

	Calculated.	Found.		
		I.	II.	III.
C	81.08	80.71	...	...
H	6.30	6.90	...	...
N	12.61	...	12 64	12.56

Hydrochloric acid salt, $C_{13}H_9N_2 : C_2H_5HCl, 3H_2O$.—Formed by dissolving the base in warm hydrochloric acid; crystallises in fine short colorless needles, easily soluble in water. It is decomposed by heating to slightly over 100° C.

Anhydro-benzdiamido-benzene.	Ethyl-anhydro-benzdiamido-benzene.	Allyl-anhydro-benzdiamido-benzene.	Amyl-anhydro-benzdiamido-benzene.	Dimethyl-anhyd do-benzene h
Melting point 287° C. Short monoclinic prisms insol. in H_2O, benzene, and chloroform; sol. in alcohol and glacial acetic acid.	Melting point 81° C. Slightly sol. in H_2O and petrol. ether; very sol. in alcohol, benzene and chloroform.	Melting point 87° C. Coarse needles. Slightly sol. in H_2O; sol. in alcohol and benzene.	Fine rhombic tables.	Melting point 15 in H_2O; difficu cold alcohol and in hot alcohol.
$C_{13}H_9N_2H : HCl.$ Out of acid solution. Needles rather difficulty sol. in H_2O.	$C_{13}H_9N_2 : C_2H_5HCl, 3H_2O.$ Short fine needles, easily sol. in H_2O.	$C_{13}H_9N_2 : C_3H_5HCl, H_2O.$ Melting point 129° C. Fine needles.	$C_{13}H_9N_2 : C_5H_{11} . HCl.$ Long needles. Difficultly sol. in H_2O.	$C_{13}H_9N_2 : (CH$ Large tables, e H_2O.
$C_{13}H_9N_2H : HCl, 2H_2O.$ Out of neutral solution.				
$C_{13}H_9N_2H : HCl, 3H_2O.$ Out of alcohol. Fine needles.				
$(C_{13}H_9N_2H : HCl)_2PtCl_4.$ Yellow needles.	$(C_{13}H_9N_2 : C_2H_5HCl)_2PtCl_4$ Yellow precipitate, slightly sol. in H_2O and alcohol; insol. in benzene and chloroform.	$(C_{13}H_9N_2 : C_3H_5HCl)_2PtCl_4$ Grayish yellow needles. Sol. in H_2O.		$[C_{13}H_9N_2 : (CH_3$ Orange yellow Slightly sol. in H
$C_{13}H_9N_2H : HI, H_2O.$ Straw colored needles, rather difficultly sol. in cold water.		$C_{13}H_9N_2 : C_3H_5HI.$ Melting point 178° C. Yellow needles. Difficultly sol. in H_2O and alcohol.	$C_{13}H_9N_2 : C_5H_{11}HI.$ Light yellow needles. Sol. in H_2O.	$C_{13}H_9N_2 : ($ Melting point 280 Sol. in hot H_2O a hol.
$C_{13}H_9N_2H : HI, I_2.$ Fine plates, red by transmitted, green by reflected light; sol. in alcohol and glacial acetic acid.				$C_{13}H_9N_2 : (C$ Melting point 140 red brown needl hot alcohol and g acid.
$(C_{13}H_9N_2H)_2H_2SO_4, 2H_2O$ Fine needles. Difficultly sol. in H_2O.		$C_{13}H_9N_2 : C_3H_5, H_2SO_4.$ Melting point 166°-170° C. Fine tables. Sol. in H_2O and alcohol.	$C_{13}H_9N_2 : C_5H_{11}, H_2SO_4, 2H_2O$ Long needles. Sol. in H_2O.	$C_{13}H_9N_2 : (CH_3)_2$ Thick tables; e H_2O.
$C_{13}H_9N_2H : HNO_3.$ Fine needles. Difficultly sol. in H_2O.	$C_{13}H_9N_2 : C_2H_5HNO_3, H_2O$ Melting point 155° C. Needles. Quite sol. in H_2O.	$C_{13}H_9N_2 : C_3H_5HNO_3, H_2O$ Melting point 136°-140° C. Colorless tables, monoclinic. Quite sol. in H_2O.		$C_{13}H_9N_2 : (CH$ Colorless crystals in H_2O.

ydro-benzdiami- ne hydroxide.  t 152° C. Insol. fficultly sol. in nd alkalies; sol. .	Diethyl-anhydro-benzdiamido-benzene hydroxide.  Melting point 136° C. Monoclinic prisms. Insol. in H_2O and alkalies, sol. in alcohol, benzene and chloroform.	Diallyl-anhydro-benzdiamido-benzene hydroxide.  Melting point 62°-63° C. Large monoclinic tables. Difficultly sol. in petrol. ether; easily sol. in alcohol, benzene and chloroform.	Diamyl-anhydro-benzdiamido-benzene hydroxide.  Melting point 92°-93 C. Large crystals. Insol. in water; sol. in all cohol, benzene and chloroform.
$CH_3)_2Cl, H_2O$. , easily sol. in	$C_{13}H_9N_2:(C_2H_5)_2Cl, 2H_2O$. Large stable tables out of neutral solution; easily sol. in H_2O. $C_{13}H_9N_2:(C_2H_5)_2Cl, HCl, xH_2O$. Hygroscopic crystalline mass, out of acid solution. Very sol. in H_2O.	$C_{13}H_9N_2:(C_3H_5)_2Cl, 4H_2O$. Large tables. Double iodide. $\{C_{13}H_9N_2H:HI\}$ $\{C_{13}H_9N_2:(C_3H_5)_2I\}$ Long yellow needles. Sol. in H_2O.	$C_{13}H_9N_2:(C_5H_{11})_2Cl, HCl, H_2O$. and $C_{13}H_9N_2:(C_5H_{11})_2Cl, HCl, 3H_2O$. Large crystals. Sol. in H_2O.
$CH_3)_2Cl]_2PtCl_4$. ow precipitate, in H_2O.	$[C_{13}H_9N_2:(C_2H_5)_2Cl]_2PtCl_4$. Orange yellow precipitate. Very slightly sol. in H_2O.	$[C_{13}H_9N_2:(C_3H_5)_2Cl]_2PtCl_4$. Fine orange plates. Insol. in H_2O and alcohol.	$[C_{13}H_9N_2:(C_5H_{11})_2Cl]_2PtCl_4$. Pale orange yellow precipitate.
$N_2:(CH_3)_2I$. 280° C. Needles. $_2O$ and hot alco-	$C_{13}H_9N_2:(C_2H_5)_2I, H_2O$. Pale straw-colored needles and prisms. Sol. in H_2O.	$C_{13}H_9N_2:(C_3H_5)_2I$. Melting point 212° C. Monoclinic prisms, straw-colored. Sol. in H_2O.	$C_{13}H_9N_2:(C_5H_{11})_2I$. Straw-colored needles. Sol. in H_2O.
$:(CH_3)_2I, I_2$. 140.5° C. Long eedles. Sol. in nd glacial acetic	$C_{13}H_9N_2:(C_2H_5)_2I, I_2$. Melting point 154° C. Brown red needles and tables. Sol. in alcohol and glacial acetic acid.	$C_{13}H_9N_2:(C_3H_5)_2I, I_2$. Melting point 101° C. Dark red needles, and fine green glittering plates. Sol. in alcohol and glacial acetic acid.	$C_{13}H_9N_2:(C_5H_{11})_2I, I_2$. Melting point 111°-112° C. Dark crystals. Sol. in hot alcohol, glacial acetic acid, CS_2, chloroform and benzene.
$H_3)_2HSO_4, H_2O$. ; easily sol. in	$C_{13}H_9N_2:(C_2H_5)_2HSO_4, H_2O$. Large thick tables; easily sol. in H_2O.	Picrate. $C_{13}H_9N_2:(C_2H_5)_2OC_6H_2(NO_2)_3$. Melting point 118° C. Small yellow prisms. Difficultly sol. in H_2O and alcohol.	
$(CH_3)_2ONO_2$. stals; easily sol.	Nitrate is an oil.		$C_{13}H_9N_2:(C_5H_{11})_2ONO_2, HNO_3$. Melting point 90° C. Thin broad needles. Sol. in H_2O.

Analysis:

I. 0.381 gram dry salt gave 0.2165 gram AgCl.

II. 0.142 gram dry salt gave 0.0786 gram AgCl.

Calculated for $C_{13}H_9N_2 : C_2H_5HCl$.		Found. I.	II.
Cl	13.73	14.04	13.69

III. 0.1683 gram air-dried salt lost at 100° C. 0.0263 gram H_2O.

IV. 1.0104 gram air-dried salt lost over H_2SO_4 in six days 0.17 gram H_2O.

Calculated for $C_{13}H_{14}N_2 : HCl, 3H_2O$.		Found. III.	IV.
H_2O	17.28	15.63	16.82

Double platinum chloride, $[C_{13}H_9N_2 : C_2H_5HCl]_2PtCl_4$.—Thrown down from a solution of the hydrochloric acid salt by platinic chloride as a very fine yellow crystalline precipitate; insoluble in petroleum ether, benzene, ether, chloroform, and but slightly soluble in hot water, alcohol, and acetone.

Analysis:

I. 0.1757 gram gave 0.0401 gram Pt.

II. 0.6994 gram gave 0.1595 gram Pt.

Calculated for $[C_{13}H_{14}N_2 : HCl]_2PtCl_4$.		Found. I.	II.
Pt	22.89	22.82	22.81

Nitric acid salt, $C_{13}H_9N_2 : C_2H_5HNO_3, H_2O$.—Formed by dissolving the base in warm dilute nitric acid, and crystallises in beautiful, fine, colorless needles, whose melting point is 155° C.

Analysis:

I. 0.319 gram lost at 100° C. 0.0188 gram H_2O.

II. 0.2709 gram melted salt gave 0.0391 N.

Calculated for $C_{13}H_9N_2 : C_2H_5HNO_3, H_2O$.		Found. I.
H_2O	5.94	5.89
Calculated for $C_{13}H_9N_2 : C_2H_5HNO_3$.		Found. II.
N	14.73	14.44

Derivatives of anhydro-benzdiamido-benzene.—The annexed table presents a comparative view of all the derivatives of anhydro-benzdiamido-benzene, and is compiled from Prof. Hübner's

articles in the Annalen der Chemie, **208,** 305, and **210,** 347 ff., dissertations by Dr. C. S. Merrick (Göttingen, 1882), and Dr. F. Rinne (Göttingen, 1883), and the writer's own researches.

Dr. Merrick's work calls attention to the different hydrochloric acid salts of the anhydro-base and the peculiar double iodide of the anhydro-base and the diallyl derivative, and also the existence of two allotropic forms of the hydriodic salt of the diallyl derivative. One of these crystallises out of petroleum ether, and the other out of chloroform, though after being once crystallised, each could be recrystallised in either solvent without losing its characteristic form. That crystallised out of chloroform is unstable, and gradually becomes opaque. Both forms were measured by Dr. Rinne, and are monoclinic, the former approaching very nearly the rhombic system, and showing the forms ∞P and oP. — $\beta = 89° 35' 37''$; the latter showing oP, $\infty P\infty$, $+ P$, $- P$ and $\beta = 85° 15'$.

Laboratory of the Central University, Richmond, Ky., *October*, 1883.

ON THE CONDUCT OF MOIST PHOSPHORUS AND AIR TOWARDS CARBON MONOXIDE.

By Ira Remsen and E. H. Keiser.

In a paper recently published[1] we described some experiments which led us to the conclusion that when a mixture of carbon monoxide and air is brought in contact with moist phosphorus there is no oxidation of the monoxide. This conclusion is directly opposed to that reached by Leeds[2] and by Baumann,[3] according to whom the oxidation is easily effected. If these chemists are right, it follows that when moist phosphorus acts upon oxygen, something is formed which is distinct from free oxygen and from ozone. To this the name active oxygen has been given. Since our paper appeared, both Leeds[4] and Baumann[5] have published the results of new experiments, and, as

[1] This Journal, **4**, 454. [2] Journal American Chemical Society, **1**, 322.
[3] Zeitschrift für physiologische Chemie, **5**, 250. [4] Chemical News, **48**, 25.
[5] Berichte der deutschen chemischen Gesellschaft, **16**, 2146.

we suggested that their error might be due to the action of ozone on organic substances present, such as cotton wool, rubber, corks, etc., they have carefully avoided such contact. Leeds finds no occasion to modify in the slightest degree his first statement on the subject. Baumann, however, who has taken great care in the construction of his apparatus, and whose paper gives clear indications of accurate work, obtains results which differ in some respects from those described by him in his first paper.[1] In the latter, in speaking of the passage of the mixture of air and carbon monoxide over the phosphorus, he says: "das vorgelegte Barytwasser wird schon nach kurzer Zeit trübe und im Laufe einer Stunde bildet sich ein reichlicher Niederschlag von kohlensaurem Baryt." In this experiment the gases were used in the proportion three volumes of oxygen to one of the monoxide. The whole description is such as to leave upon the mind of the reader the impression that the oxidation is very easily effected. In his last paper Baumann is much more cautious, and, though he still insists that the carbon monoxide is oxidised, the extent of the oxidation appears to have been much less than in the first experiments. Instead of getting an abundant precipitate (reichlicher Niederschlag), only a small one was obtained, and the formation of this required a much longer time, as appears from the following passage: "Nach den ersten zwei Stunden zeigte sich schon eine deutliche Trübung . . . die von da ab stetig zunahm: da der Niederschlag hauptsächlich im Innern der Zuleitungsröhre . . . abgeschieden wurde, wurde letztere nach weiteren 10 Stunden verstopft."

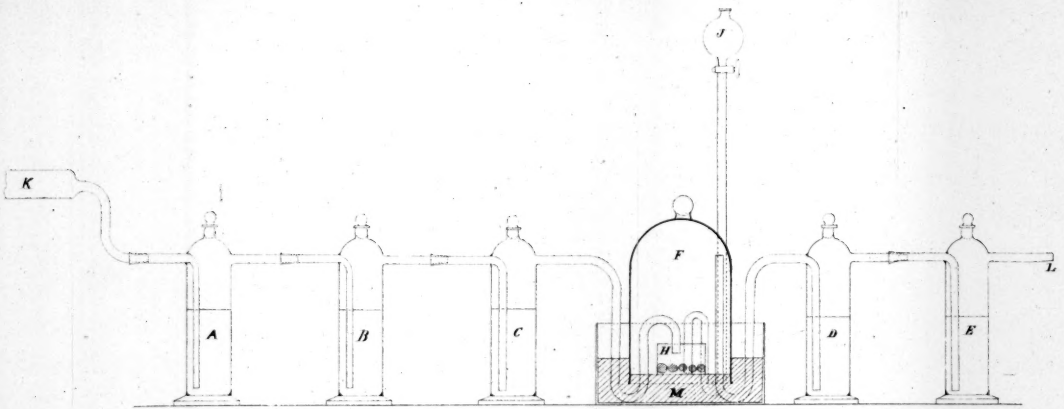
Another point which arrests attention when the paper is read critically is this, that in order to get evidence of oxidation very large volumes of air mixed with a little monoxide are passed over the phosphorus. In one case 200 cc. of the monoxide are admitted every two hours. In another the author speaks of using 700 cc. of the monoxide "in starker Verdünnung mit Luft," the passage requiring 15 hours. The amount of carbon dioxide obtained was 0.0366 gram, or 2.6 per cent. of the monoxide was oxidised. In still another experiment, a mixture consisting of 30 litres of air and 2.45 litres of the monoxide occupied 12 hours in passing the phosphorus, the amount of carbon dioxide obtained being 0.0646 gram, representing the oxidation of 1.3 per cent. of the monoxide.

[1] *Loc. cit.*

Of course there can be no objection to using large volumes of air, provided it can be shown by blank experiments that no error is introduced in consequence, and this Baumann appears to have done. Speaking of passing air alone through the apparatus he says: "Hält man den Luftstrom so, dass . . . in der Secunde nicht mehr als zwei bis drei Blasen hindruchtreten, so entsteht . . . auch nach mehreren Tagen nicht mehr als eine ganz leichte Trübung von phosphorsaurem resp. phosphorigsaurem Baryt."

Passing now to Leeds's new experiment, but a few words will be necessary. This writer filled a glass-stoppered 10-litre flask with a mixture of equal parts of carbon monoxide and air, and allowed the mixture to stand in contact with moist phosphorus for six days. Then the glass stopper was removed, replaced by a cork, and, the mouth of the vessel being placed under mercury, the gases were displaced and passed through baryta water. A precipitate representing 0.0155 gram of carbon dioxide was obtained. There is one source of error in this experiment which should be noted at once. It is clear that by standing for six days in the tightly closed vessel, the oxygen of the air must have been completely used up, so that the gases were necessarily under diminished pressure. Apparently, in taking out the glass stopper for the purpose of introducing the cork, no precautions were taken to prevent access of ordinary air, and a considerable volume of ordinary air must have entered; not enough certainly to give the quantity of carbon dioxide obtained, but enough to cause a perceptible precipitate in the baryta water. Another source of error, however, much more serious than this, and quite sufficient to account for the result, has since been discovered by us.

Although we felt convinced of the accuracy of our first work and the correctness of the result, we have nevertheless subjected the work to a careful revision. Working with the precautions previously used, we have obtained exactly the same results as at first. On studying Baumann's paper, however, it seemed to us possible that there might be a slight oxidation, so slight as to escape notice when comparatively small volumes of the gases are used. Now, in most of our first experiments small volumes were used, and we therefore felt it incumbent upon us to go over the work, using larger volumes. We first passed thoroughly purified air through an apparatus which was so arranged as to prevent all contact of ozone with organic substances. The current was fully as slow as that in


K
A
B
C
F
J
H
M
D
E
L

Baumann's experiments, and the gases, after passing out of the ozonising vessel, were washed with a rather larger quantity of water than was used by Baumann. A cloudiness began to appear in the baryta water after six or eight litres of air had passed through, and this increased constantly, until when 25 to 30 litres had passed in 12 to 15 hours a distinct precipitate, not a mere turbidity, was in the vessel containing the baryta water. The precipitate was carefully examined with reference to the presence of phosphorus compounds, but not a trace could be detected. The experiment was repeated with the same result. It is clear, therefore, that in spite of Baumann's explicit statement, there is some source of carbon dioxide independent of carbon monoxide, and before accurate experiments can be made this source must be discovered and if possible avoided.

Karsten[1] has shown that when air alone comes in contact with the organic matter of corks and connectors, carbon dioxide is formed, and that if a large volume of air is first freed from carbon dioxide and then passed through lime water, a precipitate is formed, unless all contact with organic matter is prevented. Storer[2] has recently confirmed this observation. It hence seemed possible that the carbon dioxide obtained from the air in our experiment might be formed either from the organic matter in the air or by the action of the air on the rubber connectors and corks of the wash bottles used in purifying it, and our next step was to so arrange our apparatus as to absolutely exclude all organic matter. This was effected by means of an apparatus illustrated in outline in the figure. The wash bottles *A*, *B*, *C*, *D*, *E*, were made for us by a skillful glassblower. They are fitted with glass stoppers, and the escape tube of each fits air-tight into the entering tube of the next one by means of a ground glass joint. The tube, *K*, only partly represented in the figure, is about 14 inches long and of hard glass. The vessel, *F*, is an ordinary bell jar, holding about one and a quarter litres. This is held in position on mercury contained in a crystallising dish. Upon the mercury floats a smaller vessel, in which the phosphorus is placed. The tube from the last wash bottle through which the air is passed before it comes in contact with the phosphorus is bent so as to pass beneath the edge of the bell jar, then up into the closed space above the mercury, and then down towards the phosphorus. The tube through which the

[1] Poggendorff's Annalen, **115**, 348. [2] This Journal, **5**, 69.

carbon monoxide is passed into the vessel is arranged in the same way. A long funnel tube, *J*, is bent in a similar way, but reaches down to the bottom of the dish containing the phosphorus. By means of it the phosphorus can be covered with water or uncovered, as may be desired, without disarranging the apparatus. The tube through which the gases pass out of the bell jar is bent like the two already referred to, with the exception that it is not directed downward after entering the vessel, but is allowed to project nearly to the top of the space. All joints which are not of ground glass are carefully fitted by means of gypsum.

This is the apparatus exactly as it was used in a number of experiments with air alone. The method of experimenting was as follows: The air was contained in a gasometer holding 30 litres. From this it was passed slowly, at the rate of about two or three bubbles per second, into the hard glass tube, *K*, containing copper oxide heated to dull redness; then through the three wash bottles, the first two containing caustic soda, and the last one baryta water. It was then passed into the bell jar containing the phosphorus. Care was taken to keep the air in this vessel as near 24° as possible, and the white fumes indicating the action of the phosphorus were always abundant during the course of an experiment. The amount of phosphorus exposed, that is, not covered by water, varied from 20 to perhaps 70 or 80 grams, the usual amount being between 20 and 30 grams. From the bell jar the ozonised air with whatever it contained passed through the wash bottle, *D*, containing from 30 to 40 cc. of pure distilled water, and then into the concentrated baryta water. The last bottle, *E*, containing the baryta water was connected with a tube containing caustic potash to protect it from the ordinary air.

We cannot see how any exception can be taken to the apparatus used by us, or to the method of conducting the experiments. Nevertheless, working under what appear to us to be perfect conditions, we obtained exactly the same result as we had obtained in the first experiments with air, viz. the air alone when passed for a sufficient length of time gave a precipitate in the last bottle. Ten litres of air always cause a distinct turbidity, and twenty to thirty give a precipitate. As there was no possible source of error, it follows that the carbon dioxide obtained must have come from carbon contained in the phosphorus. There is no escape from this conclusion. That there should be carbon in phosphorus

is not surprising when we consider the method of manufacture and the fact that boron, silicon, iron, etc., which are made by similar methods, all contain small quantities of this element. Indeed, the presence of carbon in the phosphorus as it is at first obtained is well known, and, in the purification process adopted, chromic acid is used for the purpose of removing it. *A priori* we would hardly expect the process of purification to be complete, and our experiments furnish the proof that it is not.

Whether the carbon is present in the phosphorus in chemical combination or not is a question difficult to answer. We can only say that the phosphorus used by us appeared to be perfectly homogeneous. There was no evidence of the presence of particles in it. Its solution in carbon bisulphide was clear, and on standing nothing whatever was deposited. Some of the phosphorus which we used had been carefully redistilled by us. This made no difference in the result. These facts lead us to believe that the carbon is in chemical combination with the phosphorus.

We have made some attempts to estimate the quantity of carbon present, but have not been successful. A simple way to show its presence is to burn a piece of phosphorus in a small porcelain dish floating on water under a bell jar fitted with a glass stopcock. After the combustion is over, the vessel is allowed to stand for some time until the white fumes have entirely disappeared. The gas is then passed through water and finally into baryta water, where a not insignificant precipitate is invariably formed. The air in the bell jar must, of course, be purified. As the vessel is lifted only far enough to permit the introduction of the dish with the phosphorus, and this operation is performed instantaneously, the amount of carbon dioxide introduced with the air can be only infinitesimal.

The complete oxidation by means of chromic acid of a weighed quantity of phosphorus, and estimation of the carbon dioxide formed, gave unsatisfactory results, for the reason that it was impossible to regulate the action and at the same time secure complete oxidation of the phosphorus. With concentrated solutions the action is liable to become very violent unless the temperature is kept low. By means of the experiments with chromic acid we were able to demonstrate the presence of the carbon by the formation of a precipitate of barium carbonate, but though the precipitate was weighed in a few cases, the results are of little value, as the action was evidently incomplete.

Similar experiments with nitric acid were equally unsuccessful as quantitative analyses, though they also clearly showed the presence of carbon.

Finally an apparatus was arranged similar to that used for making phosphorus pentoxide on the small scale. The combustion was effected in pure air, and after being thoroughly washed the gases were passed through baryta water. Again a precipitate was formed, but the operation was far from perfect, owing to the formation of a considerable quantity of red phosphorus, and to imperfect oxidation.

For the present we have given up the attempt to estimate the quantity of carbon in phosphorus, and content ourselves with having proved beyond question that it is present in sufficient quantity to interfere with such delicate experiments as those upon the oxidation of carbon monoxide.

We now made some experiments with the object of determining how far changes in the amount of phosphorus exposed in the ozoniser perceptibly changed the amount of barium carbonate formed. We found that the amount of the precipitate is plainly influenced by the rate of passage of the gases, the temperature, and the amount of phosphorus exposed, but that, if the temperature is between 20 and 25°, the rate of passage of the air about two or three bubbles per second, and the amount of phosphorus exposed from 20 to 30 grams, a slight precipitate is always formed by 10 litres of air, and that 25 to 30 litres give a very decided precipitate.

It does not of course follow from the facts above described that carbon monoxide is not oxidised by air in the presence of moist phosphorus, but it is clear that in experiments undertaken for the purpose of deciding the question, allowance must be made for the presence of carbon in the phosphorus. The amount of allowance to be made cannot be determined with accuracy, for the amount of phosphorus exposed cannot be perfectly controlled in the apparatus used. The best way to reach a positive conclusion is to perform parallel experiments under as nearly the same conditions as possible, one with air alone, the other with air and carbon monoxide. If the vessels in which the precipitates are formed are of the same shape and size and each contains the same amount of baryta water, we can judge with a fair degree of accuracy whether a larger precipitate is formed in one case than the other.

In making these comparisons about 25 litres of air were first passed through the apparatus, the conditions being carefully noted. The bottle containing the precipitate formed was removed at the end of the operation, instantly stoppered and placed aside for comparison. The water was then removed from the wash bottle, and replaced by fresh distilled water, a new bottle attached in the place of *E*, and after passing about a litre of pure air through the apparatus, the necessary quantity of baryta water filtered rapidly through a plaited filter into the wash bottle. Now the experiment was repeated with the difference that during the passage of the 25 litres of air, a very slow current of carefully purified carbon monoxide (made from pure sulphuric and formic acids) was passed through three wash bottles like those used for the air and containing the same substances, and then, through the tube described above, brought into the presence of the phosphorus and air. The rate of the current was so regulated that, during the time of the experiment, which varied in different cases from three to eight hours, three litres of the monoxide were used. The same slow formation of a precipitate was noticed when the carbon monoxide was used as in the case of air alone. At the end of the operation we were unable to distinguish any difference between the amounts of the small precipitates formed. In neither case did this amount appear to be as great as that found by Baumann. The precipitates were too small to permit of accurate filtering and weighing, if we consider the nature of the liquid in which they were present. Comparing their size with that of certain larger precipitates which we did weigh, we estimated that they could not possibly weigh more than one to two milligrams. If there was any difference between them it could not have amounted to more than a small percentage of the total weight, and, as already said, no difference was apparent. The only conclusion which we can draw is, as we claimed in our first publication on this subject, that carbon monoxide is not oxidised by air in the presence of moist phosphorus.

The precipitate obtained by Leeds, which he ascribed to oxidation of the carbon monoxide, must have been due mainly to the oxidation of the carbon in the phosphorus. We have shown that the amount of carbon dioxide formed by burning phosphorus in a few litres of pure air is considerable; quite enough, we should judge, to give a precipitate as large as that obtained by Leeds.

The fact that Baumann obtained precipitates when working with large volumes of air is easily understood; but that they should have been as large as they were is not easily explained. That only a slight turbidity should have been obtained after several days, on passing air alone through the apparatus, is beyond our comprehension.

That in our first experiment we should have obtained no evidence of the presence of carbon is due to the fact that we worked with small volumes of the gases. In those cases in which relatively large volumes were used the slight cloudiness produced was disregarded, as the same result was obtained with air alone. We are further inclined to think that the moist asbestos through which the gases were passed may have retained a small quantity of the carbon dioxide. We have found that this method of filtering is quite superfluous, and that the water in the small wash bottle is sufficient to retain all traces of phosphorus compounds. Phosphorus could never be detected in the precipitate of barium carbonate, and, indeed, when the current was as slow as usual, phosphorus compounds were not found in the first wash bottle.

Although our experiments have cost us a great deal of time and labor, the apparatus finally used is simple and the experiments may be repeated with comparatively little trouble. We therefore hope that others who may be interested in the subject may find the time to repeat them. It is, however, absolutely necessary that all the precautions mentioned by us be taken.

It certainly appears remarkable that carbon monoxide is not oxidised by air in the presence of moist phosphorus where the formation of ozone is constantly taking place. If our ordinary conceptions in regard to this process are correct, the phosphorus splits up the molecules of oxygen and unites with some of the atoms thus set free, while other oxygen atoms rearrange themselves in the form of ozone molecules. There should, according to this conception, be free atoms of oxygen in the immediate vicinity of the phosphorus, and the first thought would naturally be that an unsaturated compound like carbon monoxide must be oxidised. That it is not is, however, quite in accordance with its conduct towards ozone during the transformation of the latter into ordinary oxygen. One of us (R.) has shown[1] that, if carbon monoxide be mixed with ozone, and the mixture passed through a tube heated

[1] This Journal, **4**, 50.

to about 300°, a temperature sufficiently high to transform all the ozone into oxygen, no oxidation of the monoxide takes place. In this experiment we have conditions exactly the opposite of those involved in the phosphorus experiment. In both cases, however, according to the prevailing notions, free atoms of oxygen ought to be formed and to exist in the interval, however brief it may be, between the breaking up of the ozone and the formation of oxygen or the splitting up of the molecules of oxygen and the formation of ozone.

Why carbon monoxide is not oxidised by ozone itself under ordinary circumstances is a question which it is impossible to answer in the present state of our knowledge; still less can we imagine a reason for the fact that it is not oxidised by the gases formed when ozone is broken up by heat, nor by those formed during the production of ozone by the action of phosphorus on moist air.

There is at present then only one experiment on record which seems to show that by starting with ordinary oxygen this can be so changed as to acquire the power to oxidise carbon monoxide at lower temperatures. This is the experiment of Baumann[1] with palladium hydrogen. In view of the fact that Traube has shown[2] that palladium and hydrogen dioxide together can readily oxidise the monoxide, an observation which we have confirmed,[3] and that hydrogen dioxide is formed, though apparently in small quantity, by the action of palladium hydrogen on air and water, the question as to the cause of the oxidising action of palladium hydrogen may fairly be regarded as an open one.

The observation of Leeds that when a mixture of carbon monoxide and air is submitted to the silent electrical discharge carbon dioxide is formed, furnishes no evidence of the formation of active oxygen, as Andrews and Tait[4] have called attention to the fact that when the silent discharge acts upon carbon monoxide alone some dioxide is formed.

[1] Zeitschrift für physiologische Chemie, **5**, 250.
[2] Berichte der deutschen chemischen Gesellschaft, **15**, 2854.
[3] This Journal, **4**, 454.
[4] Philosophical Transactions, 1860, p. 126.

ON THE CONSTITUTION OF RESOCYANIN.

By Arthur Michael.

About fourteen months ago I made the observation that a mixture of acetylacetic ether and resorcin heated with zinc chloride formed a new compound. A careful search in the literature of resorcin and acetylacetic ether failed to show that the reaction had been previously noticed, and I therefore made it the subject of an investigation. In a paper read a year ago before the Harvard Chemical Society, I described the compound and a number of its derivatives, and also a similar compound obtained from pyrogallol. Shortly afterwards the September number of the "Journal für praktische Chemie" was received, and in it I found a paper by M. Wittenberg[1] on the same subject, and also learnt that the reaction was discovered by W. Schmid[2] almost a year previous. W. Schmid's paper was entitled "On a new formation of Resocyanin," and the fact that I had not suspected the identity of the product from acetylacetic ether with resocyanin occasioned the oversight of his short note. Indeed, I had deduced from my work quite a different formula for the compound than that which Wittenberg and Schmid have assigned to resocyanin. I did not feel entitled, however, to publish my results, as Wittenberg evidently intended to continue his investigation. The last September number of the "Berichte der deutschen chemischen Gesellschaft" contains a paper by H. von Pechmann and C. Duisberg entitled, "On the compounds of Phenols with Acetylacetic Ether," in which these chemists describe resocyanin as a new compound under the name of β-methylumbelliferon, and are quite unaware of the previous researches of Schmid and Wittenberg. v. Pechmann and Duisberg come to the same conclusion regarding the symbol of resocyanin that I had a year previous, and I have thought that under these circumstances the analytical results I obtained might be published without it being considered an intrusion into Wittenberg's field.

My product was obtained by heating equal weights of acetylacetic ether, resorcin and zinc chloride until the evolution of a gas was noticed, when the reaction proceeded without further heating.

[1] Journal für prakt. Chemie [2], **26**, 66. [2] *Ibid.* [2], **25**, 81.

After the effervescence ceased the mixture was heated for 15 minutes, and then poured in cold water. The crystalline product is best purified by dissolving in hot alcohol, filtering, treating with bone black, and several crystallisations from alcohol. Schmid found carbon dioxide as the only gas given off in the reaction. I think that besides this gas a small amount of ethylene is evolved; at least a gas which is not absorbed by lime water, and is by bromine.

I. 0.2626 gram of substance, dried at 110°, gave 0.6545 gram of CO_2 and 0.1131 gram of H_2O.

II. 0.2536 gram of substance, dried at 110°, gave 0.6266 gram of CO_2 and 0.1121 gram of H_2O.

III. 0.2213 gram of substance, dried at 110°, gave 0.5535 gram of CO_2 and 0.954 gram of H_2O.

	Theory for $C_{10}H_8O_3$.	Found. I.	II.	III.
C	68.18	67.98	68.35	68.21
H	4.54	4.78	4.98	4.78

For comparison the results of Schmid's, Wittenberg's and v. Pechmann and Duisberg's analyses are stated:

	v. Pechmann and Duisberg.		Schmid.	Wittenberg.		Theory for $C_{21}H_{18}O_4$.
C	68.14	68.3	68.62	68.65	68.67	68.85
H	4.7	4.7	4.96	4.94	4.92	4.91

It will be noticed that while v. Pechmann and Duisberg's, and my own analyses, agree well with the formula $C_{10}H_8O_3$, those of Schmid and Wittenberg agree better with the formula of resocyanin assigned by these chemists.

The only properties of resocyanin noticed which have not been already mentioned were, that the white powdered substance is fluorescent—this is particularly noticeable when it is enclosed between two watch-glasses; and that an alcoholic solution of the substance, allowed to cool in a very quiet place, solidified to long, white needles, occupying the whole vessel, which, when rubbed, or even if the vessel is shaken, were rapidly changed into the prismatic form, not occupying one-fifth of the space taken up by the other modification.

Acetyl resocyanin was prepared by the action of acetic anhydride and fused sodium acetate on resocyanin. It remained unchanged when heated with acetic anhydride in a closed tube. My

observations on this compound agree closely with those of Wittenberg.

0.2296 gram of substance gave 0.5594 gram of CO_2 and 0.1013 gram of H_2O.

	Theory for $C_{10}H_7O_2(C_2H_3O)$.	Found.
C	66.05	66.46
H	4.58	4.90

To obtain the methyl derivative of resocyanin, that compound was dissolved in methyl alcohol containing methylsodium oxide, and an excess of methyl iodide added. After standing 12 hours, white needles separated from the clear solution, and the reaction was completed by heating for one-half hour at 100°, when the solution solidified on cooling. The substance was treated with cold dilute sodium hydrate, and the insoluble residue purified by crystallisation from hot alcohol.

0.2165 gram of substance gave 0.5496 gram of CO_2 and 0.1068 gram of H_2O.

	Theory for $C_{10}H_7O_2(CH_3)$.	Found.
C	69.46	69.25
H	5.26	5.48

This substance crystallises from hot alcohol on cooling in long white needles, melting at 158°–159°. The substance is insoluble in cold alkalies, but on warming a solution is effected, from which the addition of an acid precipitates the original substance. According to v. Pechmann and Duisberg, the methyl derivative, on boiling with alkalies, takes up water, passing over into the salt of an acid.

Resocyanin treated with nascent hydrogen takes up hydrogen. For this purpose it was dissolved in aqueous sodium hydrate, and treated with sodium amalgam until a drop of the reduced liquid poured into water failed to cause the characteristic blue fluorescence of resocyanin. The addition of acids to the alkaline solution gave a half-solid white precipitate, which soon solidified. For purification it was crystallised several times from dilute alcohol.

0.1970 gram of substance, dried at 110°, gave 0.4902 gram of CO_2 and 0.0971 gram of H_2O.

0.2425 gram of substance, dried at 110°, gave 0.6057 gram of CO_2 and 0.1170 gram of H_2O.

	Theory for $C_{10}H_{10}O_2$.	Theory for $C_{10}H_9O_2$.	Found.	
C	67.41	67.80	67.82	68.16
H	5.61	5.08	5.42	5.36

This reduction product is insoluble in hot water, soluble in hot dilute alcohol, and separates on cooling as slender prisms with straight end-faces. In order to obtain the correct melting point it is necessary to heat a paraffin bath almost to the melting point of the substance—about 255°—as prolonged heating below its melting point causes it to blacken before melting. The melting point obtained in this manner was 257°–259°. Dilute alkalies dissolve the substance in the cold, and the addition of an acid precipitates the original substance. The alkaline solution does not show any fluorescence, but became slightly fluorescent on standing exposed to the air. This indicates that resocyanin was re-formed by oxidation.

The reduced substance is converted by the action of acetic anhydride and sodium acetate into an acetyl derivative. The product of the reaction was extracted with water, and the insoluble residue crystallised several times from alcohol.

0.2325 gram of substance, dried at 110°, gave 0.5625 gram of CO_2 and 0.1126 gram of H_2O.

	Theory for $C_{10}H_9O_3(OCCH_3)$.	Theory for $C_{10}H_8O_2(OCCH_3)$.	Found.
C	65.45	65.75	65.98
H	5.45	5.02	5.38

This compound crystallises from alcohol as colorless, glittering, rhombic prisms with macrodiagonal domes, and melts at 221°–222°. It is insoluble in boiling water, sparingly soluble in hot dilute alcohol, moderately in hot alcohol. In boiling glacial acetic acid it is more soluble than in hot alcohol. The results of the analyses of hydroresocyanin are better in accordance with the formula $C_{10}H_9O_3$ than with $C_{10}H_{10}O_3$. Although I do not consider the analytical data as settling conclusively the symbol of hydroresocyanin, it appears probable from them that the symbol of resocyanin should be doubled, $C_{20}H_{16}O_6$ instead of $C_{10}H_8O_3$, as the addition of a single atom of hydrogen could hardly result other than from the reduction of carbonyl and the formation of a pinacone. This, however, would give hydroresocyanin four hydroxyls, whereas the analysis of the acetyl product showed that the compound contains but two hydroxyls.

Wittenberg obtained resorcin from resocyanin by fluxing with potassium hydrate. My observations agree with those of v. Pechmann and Duisberg, that boiling with concentrated alkali

decomposes the substance, forming resorcin almost quantitatively. The decomposition is dependent on the concentration of the alkaline solution; and, as would seem from several experiments, also on the relative amount of alkali. Resocyanin may be boiled for several days with dilute caustic potash without undergoing decomposition. My experiments on the relation between the decomposition and quantity of alkali are very meagre, and are only several preliminary observations which I had made several days before the knowledge of Wittenberg's research caused me to discontinue my work. I found that a concentrated solution of resocyanin in potassium hydrate, in the proportion of one molecule of the former to two of the latter compound, required continued heating before a noticeable decomposition ensued, while, when these substances were taken in the proportion of one to three molecules, the resocyanin was decomposed in a few hours. What appears more striking is the observation that with the further addition of alkali the decomposition became much slower; when the compounds were taken in the proportion of one to four molecules the resocyanin was not entirely decomposed after heating for ten hours. This subject certainly merits further investigation.

Bromine[1] added in excess to resocyanin, dissolved in acetic acid, gave a precipitate which is very slightly soluble in alcohol, somewhat more soluble in hot glacial acetic acid. It crystallises in small rhombohedric crystals, melting at 240° (Wittenberg's compound melted at 250° and contained 57.14 per cent. Br.)

	Theory for $C_{10}H_8Br_2O_2$.	Found.	
Br	58.11	57.54	58.28

Bromine has no action on this compound in the cold; the substance, when allowed to stand with bromine dissolved in carbon disulphide and exposed to the sunlight for several days, was regained on evaporation of the bromine. Two grams of the tribrom compound heated with one gram of potassium hydrate dissolved in 25 cc. of water, formed a yellow solution which soon turned green. The addition of chlorhydric acid to the green solution gave a purple precipitate which, crystallised from dilute alcohol, formed clusters of white needles melting at 192°–195°.

[1] The following observations and analyses were made by my former assistant, Mr. A. M. Comey.

Resocyanin is completely oxidised in the cold, by potassium permanganate, to carbonic acid. A gram of the substance was dissolved in caustic potash, and one gram of the permanganate dissolved in water, added to the cold solution. The filtrate contained resocyanin; this was also found to be the case after addition of a second gram of permanganate. The further addition of ½ gram permanganate was sufficient to effect complete oxidation, as the solution then contained only potassium carbonate.

Equal weights of resocyanin and zinc chloride melted together form a red flux. This treated with water gave a crystalline substance, which was probably a zinc derivative of resocyanin, since it contained that metal, and when treated with chlorhydric acid gave resocyanin.

Another reaction, which was not further examined, is the action of phosphorus pentachloride dissolved in phosphorus oxychloride on resocyanin. On heating, the mass took a dark violet color, and from the filtrate obtained by pouring it into water and filtering while warm, red crystals separated, which melted between 97°–102°. These crystals boiled with water for some time gave crystals melting at 180°, which were probably not quite pure resocyanin.

It may not be amiss to make a few remarks on the theoretical considerations regarding the constitution of resocyanin that are found in Wittenberg's and v. Pechmann and Duisberg's papers. The first-named chemist has devoted several pages to the discussion of an extremely complicated structural formula, which is based solely on the analyses of the substance and its acetyl derivative. That these analyses are slightly wrong is probable from v. Pechmann and Duisberg's work, and also from the results mentioned in this note; but, at all events, v. Pechmann and Duisberg's results on the methyl derivatives, and the behavior of resocyanin towards nascent hydrogen, show the impossibility of the structural formula proposed by Wittenberg. v. Pechmann and Duisberg have suggested a more probable constitution for resocyanin, $C_6H_2\begin{cases}\diagup OH \\ O \\ \diagdown C(CH_3)\end{cases}\!\!-\!\!\begin{cases}\\ \\ CH \end{cases}\!\!-\!\!\begin{cases}\\ \\ CO\end{cases}$, but the following points need elucidation before it can be accepted: Firstly, absolute certainty in regard to the symbol of resocyanin; secondly, the properties of resacetophenon, as I have previously stated,[1] do not agree

[1] This Journal, 5, 94.

with the constitution given by Nencki, $C_6H_3(OH)_2CO—CH_3$, but better with $C_6H_4<\begin{matrix}O\\O\end{matrix}>C(OH)—CH_3$; thirdly, the results obtained by reduction indicate that resocyanin goes over into a substance with one atom more hydrogen, whereas umbelliferon on reduction adds two atoms of hydrogen and a molecule of water; and finally, absolute proof of the identity of the product obtained by oxidation of the dimethyl derivative with β-dimethylresorcylic acid.

TUFTS COLLEGE, MASS., *Nov. 19th*, 1883.

MEMORANDA OF METHODS EMPLOYED BY FISHERMEN FOR "BARKING" AND IN OTHER WAYS PRESERVING NETS AND SAILS.

BY F. H. STORER.

Seafarers are familiar with the fact that upon several foggy coasts, notably those of Scotland and of the islands north of it, as well as the coasts of Cornwall, Nova Scotia, New Brunswick, and Newfoundland, the fishermen habitually tan or "bark," as the saying is, the sails of their boats, and their nets also, in order to protect them from rot and mildew. That is to say, they are accustomed to stain the sails a dingy reddish brown color by means of materials containing tannin, such as are employed in the ordinary process of tanning leather.

The process is manifestly an old one, and references to it may be found very early in the works relating to technology. But the methods employed seem to be to the last degree empirical in most localities, and the subject appears never to have received proper attention either from professional dyers or from scientific men. It is regrettable that the systematic works on dyeing, occupied as they have been with the practical and aesthetic side of the art, have hitherto paid little heed to the rough domestic processes which are of special historic interest. It is high time that these

rough and often imperfect processes should be recorded and studied, both from the scientific and the archaeological points of view.

In seeking for what I might find printed concerning the tanning of sails I have come across several items which seem to be worthy of publication, as bearing upon the early history of the art of dyeing. I am the more especially impelled to print these notes, since no chemist, in so far as I am aware, has ever seriously considered the methods of coloring that are employed by the fishermen. Indeed, these processes have seldom been alluded to by chemists of late years. The common notion of deep-water sailors that the canvas to be stained is simply soaked in tan-pits, as hides are in the process of making leather, seems at first sight hardly probable in view of the depth of the color imparted to the sails in some localities, and of the well-known difficulty of dyeing strong, fast colors upon either linen or cotton except with the aid of mordants. Nevertheless, it appears that the sailors are very nearly right in their supposition, and that simple dipping of the sails in this sense, or, rather, boiling them in tan liquor, is a very general practice. Most of the references which I have found in books relate to it. Thus, in Wm. Lewis's "Philosophical Commerce of the Arts," London, 1763, 2, 429, it is stated that fishing nets receive a pretty durable stain from soaking in astringents. Chomel's "Dictionnaire œconomique," Paris, 1767, 2, 88, directs that nets may be colored by boiling them in tan liquor, or in a decoction of the bark of walnut roots; or the net may be rubbed with celandine or young wheat when a yellow or green color is wanted. So too, in Chambers's Cyclopædia, Dublin, 1782, Vol. 3, article Net (in Fowling). Similar directions will be found in several of the earlier dictionaries of rural affairs, and in many old books relating to country sports, such as hunting and fishing. In the "Dictionnaire de Marine," by Willaumez, Paris, 1825, p. 547, it is said that French fishermen soak their sails in a decoction of oak bark and red ochre to preserve them. James Anderson, in his "Account of the Hebrides and West Coast of Scotland," Edinburgh, 1785, pp. 336, 344, says that nets and sails are there tanned by simply soaking them in hot tan liquor from oak bark. The Encyclopædia Britannica, article Net, p. 105 of the edition of 1842, says the most usual color given to nets is the russet, which is obtained by plunging the net into a tanner's pit and letting it lie

there till it be sufficiently tinged. This is of a double service to the net, since it preserves the thread as well as alters the color. Good, in Dingler's Polytechnisches Journal, 1820, 2, 162, explains how he tans nets and sails by boiling them in tan liquor; and the same account is given in C. Mackenzie's "One Thousand Experiments in Chemistry," London, 1821, p. 508. Millett, Polytechnisches Centrallblatt, 1847, p. 1285, cited in Elsner's Mittheilungen, 1, 124, says fishermen merely soak their nets in hot tan liquor. He himself put some linen thus treated in a damp cellar and kept it for years. Wimmer, Dingler's Polytechnisches Journal, 121, 372, repeated Millett's experiment with success. H. de la Blanchère, in his "Nouveau Dictionnaire général des Pèches," Paris, 1868, p. 763, says nets are tanned to hinder them from rotting. A quantity of ground oak bark is boiled for a couple of hours in rain water, and the still boiling liquor is poured upon the dry clean net, which has been placed in a tub. The net is well kneaded in the liquor and turned several times during the day. It is then left to soak during thirty-six or forty hours; finally it is withdrawn from the liquor and dried. The operation is repeated once a year. It has become more and more common to use catechu for tanning sea nets, and to-day most of them are preserved with this material. Being much richer in tannin than oak bark, it tans the nets more strongly and preserves them better. The operation is performed in the same way by means of hot water saturated with catechu, often admixed with oak bark to lower the price a little. The tanning of lines, also, especially for sea fishing, is an important operation, both because they last longer and because they are less visible. A dead-leaf color is obtained by chopping walnut bark or oak bark fine and boiling the fragments one hour in water. The lines are placed in the vessel among the bark and left to soak twenty-four hours. They are then taken out, wrung and dried. Catechu may be substituted for the bark; it acts quicker and gives a more solid color. A dirty orange color is obtained by collecting a quantity of the plant *Chelidonium Majus* in the fields and simply rubbing the lines with the green plant, so that they may be impregnated with the juice. The lines are then dried and the process is complete. A green color is obtained from young wheat plants chopped and pounded and boiled. The lines are soaked in the liquor twenty-four hours. In addition to the foregoing, Walton is credited by de la

Blanchère with a method of dyeing lines with walnut leaves, beer and alum.

I have myself made numerous enquiries of people likely to know something about the subject, and I am greatly obliged to many persons for the information they have given me and the pains they have taken to procure information. The well-known ichthyologist, Captain Nath. E. Atwood, of Provincetown, in particular, put me in personal communication with fishermen from Nova Scotia, who in their own country had been accustomed from early youth to the barking of nets and sails. The accounts given by these men were explicit and concordant, to the effect that the bark of fir and spruce trees was collected in the woods and boiled thoroughly in water. The nets having been placed in tubs, the tan liquor was poured over them, the bark being thrown on top, and the nets were left to soak in the liquor during twenty-four hours. This operation was usually performed once a week, the common plan being to put the nets in soak Saturday night and leave them soaking over Sunday. These Nova Scotians were emphatic that nothing whatsoever was mixed with the tan liquor, or put upon the sails in conjunction with the tan. On the contrary, it was customary, they said, to use new sails in the boats for a short time before coloring them, in order that any grease or starch in or upon the sails might be washed out by rains and worked out by use. So, too, the small amount of oily matter which is habitually put upon flax to make the fibres work more easily in the process of manufacturing it into cloth is always washed out with soap and water before the twine or canvas comes to be subjected to the tanning process. They state that when the nets are in use the color soon washes out of them, and that the process has to be frequently repeated on this account. In their eyes, the purpose of the tan liquor seemed to be rather to "kill the slime" which is left upon the nets when fish are captured, than to permanently protect the twine from putrefactive influences. They said the same process was used for sails as for nets, only the sails were not soaked so often; they were dried after soaking. Immediately after dipping the sails were very dark, but the color gradually washed out of them. Nothing was ever added to fix the color, or, as one of my informants put it, "to set the tan." This same man stated that in the domestic economy of his locality the dyeing of linen articles was habitually practised, and that his people were accus-

tomed to use copperas and alum to set a variety of colors on household goods.

It may here be said that the use of copperas for dyeing fast blacks and browns, of various shades, as well as drabs and slate color, on cotton and linen, by means of decoctions of different barks, husks and leaves (such as those of the walnut, oak, maple, alder, beech, sumach, willow, pine, etc.), is common in American households from Nova Scotia to Florida. As I am assured by several friends, and as has frequently been published (compare, for example, Dr. F. R. Porcher's "Resources of the Southern Fields and Forests," Charleston, 1869, pp. 215-217), the traditional "butternut" garments accredited to the Southern soldiers during the war are said to have been dyed in this way. Porcher (p. 215) says, "Those who cannot obtain copperas use the water from one of the mineral springs, which is strongly impregnated with iron." On pp. 217 and 241 he urges that "vinegar and rusty iron will often fix colors without the aid of copperas"; and again, on p. 302, he says that "blacksmith's dust may be used in place of copperas." Others have suggested that, in default of copperas, the mere act of boiling the cotton and the dye-stuff in an iron pot, "preferably a clean one" (*i. e.* new and free from grease?), may help to fix the color; and it is not impossible that the influence of iron dissolved from the pot by acids in the dye-stuff may have been felt to a certain extent, in this sense, in some cases, to be alluded to directly, where fast colors are said to have been obtained by means of barks without using any mordant. Besides copperas, alum and blue vitriol are freely used in this country for various purposes in domestic dyeing,

Of late years catechu seems to have superseded bark in many localities. It is now freely used by fishermen both in Europe and America. I have myself known of boatmen occasionally soaking their mooring painters in a solution of it, to preserve them from decay, and I have seen simple catechu applied to the sails of boats, also, to preserve them from mildew. It was thought to serve a good purpose, though, unless pains are taken to turn the sail frequently while it is drying, *i. e.* while the catechu is undergoing oxidation, one side of the sail will be darker than the other.

J. G. Nall[1] says herring nets are usually made of a strong two-thread hempen twine, which undergoes a process of tanning in

[1] "Great Yarmouth," &c., London, 1866, pp. 290, 291, 293.

cutch, *i. e.* catechu, a solution of which gives the twine a brown hue. In the autumn the surface of the Yarmouth Denes, covered over with nets spread out to dry, has the appearance of a tan-pit. Oak and ash bark were formerly employed. Care has to be taken not to over-tan the nets, the meshes of which would become contracted and too much hardened. The nets are tanned in the beginning to preserve them from rotting, and the process is repeated at the close of the fishery in order to cleanse them thoroughly. A mackerel net will outlast several herring nets. They are neither exposed to the havoc created by the dogfish, nor to the grease with which the nets are saturated from the herrings, and which rots them rapidly unless they are continually cleaned.

On inquiry at one of the largest manufacturers of nets in Boston, I found, as was naturally to be expected, that the net makers use catechu in a very different way from the fishermen; that is to say, they fix it methodically with bichromate of potash, as would be done at a dye-house in the case of any other cotton or linen goods. By the manufacturers, the nets are steeped in a hot aqueous solution of catechu and then treated to a bath of the bichromate, whereby the color is oxidised, darkened, and "fastened" to the twine in the manner familiar to dyers. It is a process that has to be managed with care, lest the netting should be weakened. Extract of hemlock bark, they told me, might be used instead of catechu, but it would cost more. It is only the lighter nets, such as herring nets, that are stained with catechu in Boston. The heavier nets are tarred; and, according to my informant, his firm tar many more nets than they tan. It did not appear that tar and catechu are used together by the Boston dealers, as they are in some places.

It is a fact well known to dyers that linen and cotton can be stained, after a fashion, by the use of tanning materials even when no mordant is present. Bancroft[1] says: "There is a species of coloring matter diffused in greater or lesser proportions through the barks and other parts of almost all trees and shrubs, and which, without any basis or mordant, permanently dyes or stains wool, silk, cotton, and linen, of that particular kind of color which the French call *fauve* (fawn color), and sometimes *couleur de racine ou de noisette* (root or hazel-nut color). . . It is found most abundantly in the peelings, rinds, or husks of walnuts, in the roots of walnut

[1] "Philosophy of Permanent Colors," **1**, 227 of the Philadelphia edition of 1814.

trees, in alder bark, &c.; and it seems to acquire both body and permanency by attracting and combining with pure air." Domestic processes of dyeing cotton, in this sense, by simply soaking in tan liquor and ageing, are sometimes mentioned in the agricultural newspapers.[1] But in spite of this familiar knowledge, it would still be remarkable if so dark and so durable a color as is actually seen on the sails in some regions had been imparted to them by merely soaking or boiling the canvas in tan liquor. As bearing upon this point, I may cite the following sufficiently explicit statement from a very old authority.[2] For the sake of enforcing the contrast between cotton and wool the author premises that "vegetable filaments, and thread and cloth prepared from them, differ remarkably from wool, hair, silk, and other animal productions, . . . in their disposition to imbibe coloring matters." And in illustration of the fact, a special instance is noted, as follows:—"Fishing nets are usually boiled with oak bark or other like astringents, which render them more lasting. Those made of flax receive from this decoction a brownish color, which, by the repeated alternations of water and air, is in a little time discharged, whilst the fine glossy brown communicated by the same means to silken nets permanently resists both the air and the water, and stands as long as the animal filaments themselves."

Tannin of one kind or another is actually employed by dyers, not so much, perhaps, for the sake of the color it imparts by itself, as that it serves as a mordant to fix colors on cotton and flax, which could not otherwise be so well employed on these kinds of fibres. Crace Calvert,[3] for example, says of sumac that it is largely used in Yorkshire to mordant the cotton warps of mixed goods. By means of it the cotton takes the same colors as the woolen weft with vegetable dye-stuffs and with aniline colors. But it is particularly under the influence of weak alkalies that the tannins combine with vegetable fibres, and that they absorb oxygen, turn brown, and become fixed upon the cloth. As Calvert has said, on p. 311 of the work just cited, all the tannins are remarkable for the

[1] See, for example, "The Rural New-Yorker," Jan. 31, 1880, p. 80, and May 14, 1881, p. 327; also, "The Cultivator and Country Gentleman" (Albany), 1880, 45, 431.

[2] The chemical works of Casper Neumann, abridged by Wm. Lewis, London, 1759, p. 429 note.

[3] "Dyeing and Calico Printing," Manchester, 1876, p. 326.

avidity with which they absorb oxygen in presence of alkalies, being converted into bodies of various colors, green, red, brown, and black.

I find, on investigation, that methods of dyeing depending on the action of alkalies upon tannin have long been in familiar domestic use in this country; the bark of the maple, alder, chestnut, walnut, and butternut, and doubtless of other trees, being used in different localities, as well as the husks of several kinds of nuts. For example, L. Stanley, of Maine,[1] directs: "To color brown, make a dye of common alder bark. First dip the articles in this, then wring them out and dip them into weak lye. This will make the color light or dark, according to the strength of the alder dye. It is a fast color." In the "American Agriculturist" for January, 1869, two or three receipts for dyeing tan-color are given. In general, the directions are to boil black-walnut hulls to a strong liquor, into which either cotton or woollen yarn may be put and boiled for ten minutes. The yarn is then taken out and dipped in a pail of strong lime-water, and the operation repeated until the color suits; or, instead of the hulls, chestnut or walnut bark may be used, or extract of hemlock bark.[2] According to Porcher,[3] "the inner bark of the short-leaved pine (*P. tæda*) will dye cotton goods a brown color without the aid of copperas. After boiling in the solution, dip in strong lye." I have heard of alder bark and soft soap being used in domestic dyeing in Nova Scotia for coloring linen tan-color; and it is plain that the soap would exert an alkaline action in this case, even if it served no other purpose. It appears from all this that while tan liquor alone is undoubtedly used in some localities for staining canvas and twine, there are other places where the people are familiar with a true process of dyeing, dependent upon the use of alkalies in conjunction with decoctions of astringent barks. As will be seen directly, I have discovered one locality where the last-named system is said to be applied to the coloring of sails and nets.

After having been for forty years accustomed to the sight of tanned sails, and familiar with the sailor's belief that they are simply tanned as leather is, but without ever having been thrown into intimate contact with people who use tanned sails, I had the curiosity in the summer of 1882 to ask a very intelligent fisher-

[1] American Agriculturist, February 1867, **26**. 48.

[2] *Ibid.* Nov. 1868, p. 401.

[3] "Resources of the Southern Fields and Forests," p. 585; cf. pp. 215 and 217.

man on the New Brunswick coast how his comrades colored their sails, and was not a little surprised on being told of processes which, when chemically considered, mark a distinct advance on the traditional sytem of simple soaking in tan liquor. The New Brunswicker told me that his people boil the bark of spruce or fir trees in water for many hours, and finally decant the cooled liquor into a tub, where it is mixed with soft soap or with saleratus, and the sail (either hemp or cotton) is put to soak in the mixture for a couple of days. He maintained that sails thus tanned last two years longer than those not tanned, while for nets the process is deemed to be wellnigh indispensable. On my asking whether they didn't use oil with the saleratus, he answered that they did; and it was this reference to the use of oil and alkali which excited my interest in the subject, and led me to search for testimony which should corroborate his statement. It is evident from what has gone before, that in so far as relates to the use of alkalies with the tan liquor, the statements of the New Brunswick fisherman are fully supported. I have found evidence that both "lye" and soft soap are familiarly used as adjuncts to dyeing with barks, and it is well known that the conjoined use of tannin and alkali is an approved mode of operating which has long been habitual, in one form or another, in dyehouses. I have been assured, moreover, that soft soap is used in some Nova Scotian households in dyeing wool with cudbear, "to set the color and change its shade," which goes to show a practical familiarity with the use of this agent in coloring processes.

It should be explicitly said, perhaps, that I have not the least doubt that my informant was a thoroughly trustworthy person. I fully accept his statements as to the use of saleratus and soap; though of course he may have failed, and probably did fail, to correctly state certain details of the process as to ageing, dipping, and drying; but it will be noticed that in our conversation the word "oil" was first suggested by myself, and there is unquestionably a certain risk that we may have misunderstood one another in respect to this particular item. If oil is really used, as he said it was, in the process of coloring sails, the fact is one of no little interest in its archaeological bearings; it would be an important contribution to the history of chemical technology, for, considered merely as a method of dyeing, the process would then be essentially identical with the famous old East Indian method of fixing a fast red on cotton by means of madder (or its equivalent) and an oil mordant:

I mean the color known to the English as Turkey red, and to the French as *'rouge d'Andrinople.* The East Indian process, as described by the earlier investigators, is as follows: "For dyeing cotton, the Hindoos prepare an imperfect soap from oil, ashes, and animal matters. More precisely, they soak the skeins in a soapy liquor made with goat dung, oil (of stated kinds), and potash lye, obtained by leaching the ashes of certain plants; then they expose the cotton to sun and air for several days, and finally dye it with chay root (equivalent to madder), without applying previously to the cotton any alum, or acid, or saline matter."[1]

To my own mind, the verisimilitude, or, so to say, the chemical reasonableness, of the story as related to me by the New Brunswick fisherman lent strength to it, and I would have been glad to have found recorded evidence to support it, but, as has been seen already, I have practically failed to do so. It is to be noticed, meanwhile, that the soft soap employed by the New Brunswickers would naturally be of home manufacture and incompletely finished. It would be likely to contain of itself much of the emulsion of oil and alkali so useful in Turkey-red dyeing. The probabilities are strong withal that the soap is made from a more or less rancid fish oil such as Pallas[2] found in use among the Armenian dyers of Turkey red at Astrachan, and such as in more recent times has been approved an efficient agent by the Turkey-red dyers of Manchester.

In case it should turn out to be true that sails and nets are anywhere colored by means of an oil mordant, it will be of special interest to ascertain how long the process has been in use in the locality, and whence it came thither. It seems highly improbable that the method should have been copied either in America or Great Britain from the Turkey-red dyers, for it is only in recent times, comparatively speaking, that the process of dyeing Turkey red has been practised by the Western nations. It was not until the middle of the eighteenth century that it was successfully employed in France.[3] Mention is made of it as being employed in 1765, and it is admitted that the art has been successfully practised in Great Britain since 1785.[4] The details of the Turkey-red process, as imported to civilized Europe, were so tedious and compli-

[1] Mazeas, Memoires des Savans étrangèrs, 1763, **4**, 15-18.
[2] Cited by Berthollet, Elemens de l'Art de la Teinture, **2**, 161.
[3] Ure, Dict. Arts, **2**, 90.
[4] McPherson's Annals of Commerce, **3**, 433, and **4**, 95.

cated, and the scientific explanation of them was so little understood, that there is hardly the least likelihood that any feature of the process could have been transmitted by professional dyers to European and American fishermen or housewives in recent times. The very crudeness of the domestic processes above-mentioned would of itself indicate that they have not been derived from any modern dye-house. It seems far more probable that the tanning process might have originated in a primitive state of society, where the oil mordant may have been used familiarly, not only for red but for various other colors. It is in evidence that, though comparatively rarely used by the Western nations for fixing other colors than red, the oil mordant is perfectly competent to be used with a variety of other dyes beside madder and its congeners. Laugier[1] has dwelt upon the general applicability of the process for dyeing hemp, flax, and cotton. He finds it particularly applicable for yellows, for instance, as well as for reds. Beautiful shades of purple have been fixed upon cotton cloth by first mordanting with oil, as in the Turkey-red process, and then dyeing with aniline purple.[2] Indeed, the ordinary operation of "galling," employed incidentally in Turkey-red dyeing to strengthen and modify the red color, would be practically a dyeing of the cloth tan-color if it were pushed far enough. It is manifestly closely analogous to the dyeing of sails as described to me by the New Brunswick fisherman. It is known that under the influence of weak alkalies and dampness, galled cloth may absorb oxygen from the air and take on a brown color which is highly undesirable from the point of view of the Turkey red dyers. Chaptal[3] stated the matter many years since: "The astringent principle of the nut-galls unites with the oil and forms a compound which darkens on drying and is but slightly soluble in water." "It is better to choose a dry time for the process of galling, because damp air blackens the astringent principle. After having been galled, the cotton cloth should be dried promptly, in order to avoid the blackening which would injure the brightness of the red the dyer wishes to obtain." Lewis[4] long ago tried experiments on fixing blacks by means of an oil mordant, using soft soap and

[1] Dingler's Polytechnisches Journal, **47**, 278.

[2] Watts's Dictionary of Chemistry, **2**, 357; Reports by the Juries: International Exhibition of 1862, Class XXIII, p. 3. It is to be hoped that the yachtsman who may set topsails of this superb color and strive to carry them to the forefront will gain a more worthy renown than did his prototype at Actium.

[3] Memoires de l'Institut (An. VII), **2**, 291, 292.

[4] In his "Philosophical Commerce of the Arts," London, 1763, **2**, 431.

following Mazeas's directions. He appears to have obtained a tolerably good fixation, though his colors were not handsome. The oil mordant was formerly sometimes used also for preparing a color known as "Swiss pink."

In some localities fishermen preserve their nets and sails by the combined use of bark (or catechu), tar, and oil (or grease), and the process has specially interested me as possibly having some bearing upon the question of an oil mordant just now discussed. Thus, in the Encyclopædia Britannica, article Fisheries, p. 248 (of the edition of 1879), it is stated that "barking" the sails is a regular practice with the trawlers, as it is with most other fishermen in England and Scotland. The process consists in mopping them over with a composition of a solution of oak bark, tar, grease, and ochre, which acts as a good preservative of the canvas. This is done once in six or eight weeks, and a suitable place is kept for the purpose at all the important fishing stations. Captain J. W. Collins[1] states that to preserve their nets, the Newfoundland cod fishermen make a mixture of tan and tar, which is thought better than either used separately. The tan is made from spruce buds, fir bark, and birch bark (hemlock bark is not used), which are boiled together until it is sufficiently strong, when the bark is removed and tar added in the proportion of five gallons tar to two hundred gallons tan, the whole being stirred well together. Some care is necessary in applying this or else it will not be evenly distributed on the net. The custom of mixing tan and tar has doubtless been introduced from England, as it is known that the Cornish fishermen do this, pouring out their tanning liquor into large vats with coal tar, and this mixture is found to preserve the nets much longer than simple tanning. The Newfoundland nets when prepared in this manner generally last about four seasons.

Something similar is done by the Irish fishermen from Galway, a colony of whom have for a number of years been settled here at South Boston. I have received information from three different individuals with regard to the methods employed. The first witness assured a friend of mine that his people use "catechu, grease, and tar, to color their sails." He had himself forsaken the traditional practice and "would not himself put such stuff on a white sail." Some time afterward I had an opportunity to talk with an intelligent Galway woman, a domestic in a friend's house. I

[1] Bulletin of the U. S. Fish Commission, 1881, **1**, 7.

quote her words: "First they take the clean cloth. Then it is all white. Then they get some kind of oil, I don't know what, and get it all over the cloth, and then they hang it up to dry for a long while—a week or two weeks—and then the cloth is yellow, and then they put the oil on it again and hang it up to dry again—and I don't know what they do after that." I was careful not to ask any leading question, and made no effort to help on the story. She knew very well that the sails were almost black finally, but could not tell what made them black. Still later this same woman obtained the following account from the mouth of an old Galway fisherman. Take three gallons of tar and twenty pounds of fresh butter. Melt the butter in a vessel and add to it a cup of salt. If salt butter were used there would be no need of the salt. Heat the tar almost to boiling in another vessel, and slowly add to it the butter, constantly stirring meanwhile. When the two are thoroughly combined the mixture is applied to the sailcloth by the hands of the fishermen; generally six fishermen on each side of the sail. The rubbing-in by hand is deemed to be all-important, and it is commonly done in the early morning of a fine day, and the sail exposed to the sun in order that the mixture may be dried in. In good sunshiny weather the drying process is completed by sundown. At the end of a week another coating is given in the same manner, and after a couple of days the sail is fit for use. The quantity of tar and butter above given is sufficient for one of their fishing boats, which are some six or eight tons burthen. Great importance is attached both to the rubbing in and the drying. In connection with these stories I could but recall the fact that the old French name of tarred cloth was *toile grasse*.

In this category may be mentioned the Dutch method of tanning cotton herring nets, as described by Capt. Collins,[1] and stated by him to be "thought better than any other by these foreign fishermen." The tan is made by boiling catechu in water, in the proportion of one pound of the former to two and a half gallons of the latter. When it is sufficiently strong, the nets are soaked in it twenty-four hours and then dried. They are tanned and dried three times, and then soaked in linseed oil. A pound of oil is provided for each pound of net, and the nets are allowed to remain in the oil as long as any of it will be absorbed. They are then well drained and spread on the ground to dry, after which

[1] Bulletin of U. S. Fish Commission, 1881, **1**, 8.

the process is completed by tanning them once more. Nall[1] says a strong three-twist cotton cord procured from Musselburgh has lately been introduced as an experiment. It is prepared by steeping in a mixture of linseed oil and varnish and is then squeezed through rollers. This renders it stiff and smooth as wire when dried. It is afterwards subjected to the tanning process. In addition to hempen twine, a coarse Persian silk was employed in the netting used in the Dutch fisheries of the 17th century, as more durable. It was slightly pitched or exposed to the smoke of burning ash to acquire a dark color and render it less perceptible by the fish. There is a process of varnishing the silken lines used by pleasure fishermen for the purpose of keeping them dry and reelable that differs from the foregoing. As described by de la Blanchère, in his Dictionary, p. 765, the lines may either be boiled in a drying oil, or, better, a small quantity of drying oil with which some white and green paint has been mixed may be carefully rubbed upon and into the stretched line. A second coating of the varnish is laid on when the first has become dry, and the operation is repeated at intervals until the wished-for stiffness and impermeability have been obtained. De la Blanchère remarks, also, that nets are sometimes treated with tars obtained from coal, and that the fishermen commend coal tar for this purpose in certain cases, in spite of the black color and the penetrating odor it imparts to the nets. John M. Mitchell[2] reports that Irish nets are most frequently tarred instead of being barked. Tarred nets, he says, are not so durable; in direct opposition to which statement I found a strong feeling at Provincetown in favor of tar as being a much better preservative of nets than tan. Capt. Atwood was decidedly of this opinion. Until the war of the rebellion his townspeople were accustomed to use pine tar from the South; it was only when their supply of the material was cut off that they began to use coal tar. One of the Nova Scotian fishermen with whom I talked about tanning nets laid a good deal of stress on the large amount of "gum" there was in the fir bark employed. Both he and Capt. Atwood seemed to believe that this resinous matter played an important part in preserving the nets. The Boston manufacturer of nets previously alluded to said that his firm formerly used Wilmington tar, but now they used coal tar altogether. He urged that tar

[1] In his "Great Yarmouth," &c., London, 1866, p. 291, and 290 note.
[2] In his book "The Herring," Edinburgh, 1864, p. 99.

makes the net stronger, that it makes the twine more like wire, that it hardens the fibres and keeps them together so that the twine does not fray. He had heard of tar and oil being used together, linseed oil he supposed, and thought the purpose of the oil might be to soften the tar. He remarked on having no facilities for drying (ageing) the tarred nets in his Boston warehouse, and dwelt upon the fact that freshly tarred nets are liable to "heat" and spoil. To prevent them from suffering injury in this way it is customary to soak them in brine. Moreover, when tarred nets are done up into bales, salt is scattered upon each layer of the netting to hinder the package from heating. It appears that it is now customary with the fishermen on the New England coast to regularly salt down their nets when they are stowed away at the end of the fishing season. In warm weather also the mackerel fishermen are at pains to strew salt upon their nets, layer by layer, when they stow them, even for brief periods, in the seine boats; the idea being, of course, in this case to check the putrefaction of the slime and gurry with which the nets are soiled.[1]

As to other methods of protecting sails from mildew, I learn that burnettising (*i. e.* the use of a dilute aqueous solution of chloride of zinc) is sometimes practised in this vicinity. I was assured by the captain of a sea-going schooner that once when a suit of his vessel's sails seemed ruined with mildew he had them dipped, with the result that they came out white and clean, and wore well for three years. One practice is to spread out the sails of small vessels on a beach and wash them over with a mixture of whitewash and brine. Some people appear to use plain whitewash. An objection is urged, however, to the use of lime that it tends to rot the canvas, and there is probably some risk that in seeking to destroy the mildew fungus with alkalies, the growth of forms favorable for putrefaction may be promoted. To quote from Duclaux:[2] "Acid liquids are in general more favorable to moulds, to yeasts, and to mycoderms; it is only very exceptionally and only *en passant* that

[1] The modicum of truth in the old conception that "putrescent bodies exert an action on complex organisations which by themselves are not putrescent," is well illustrated by a case like this. A parcel of microdemes having established a satisfactory residence upon the animal matter with which a net is soiled, soon find the cellulose of the twine a useful addition to their food. It serves in some sort as a diluent of the highly nitrogenised ration which the slime supplies. In other words, some of the constituents of the cellulose of the fibre are involved in the reactions which occur during the fermentation, and the integrity of the twine suffers accordingly.

[2] E. Duclaux, "Ferments et Maladies," Paris, 1882, pp. 43, 45, 50.

mobile forms are found in them, *i. e.* vibrios, bacteria, or monads. These kinds appear, on the contrary, by preference, in neutral or alkaline liquids, where the moulds for their part have much trouble to live. The mould Aspergillus, for example, grows freely on bread moistened with vinegar, on the juice of lemon or slices of lemon, and on sour fruits and liquors."

I find a common impression that the sizing in new canvas attracts mildew, *i. e.* that the mildew fungus finds a fit field for its support in the sizing which has been introduced into the interstices of the canvas at the factory. To avoid this difficulty some owners of vessels prefer to bend their new sails in the autumn in order that the sizing may be "worked out" of the canvas by the autumn and winter rains, at a time, that is to say, when the weather is too cold for mildew to prosper. Old sails are said to be comparatively exempt from mildew. The time-honored and universal custom of shaking out or hoisting sails in order that they may dry after rain is one familiar method of preservation. It is precisely because drying is frequently impracticable in some climates that the tanning process is practised.

It would be well to study practically whether the method of permanently dyeing sails, either with the aid of an alkali or by means of an oil mordant, is really an effective means of shielding the canvas from the mildew fungus; and it would be of interest to determine whether the altered and oxidised oil that constitutes the mordant in Turkey-red dyeing might not of itself help to preserve sails, even if no tanning or other coloring substance were combined with it. This last question could perhaps be answered at once, even now, by persons who have had experience with the use of Turkey red cloths in damp situations. It is not unfair to suppose that the oil mordant might be useful of itself, since it would probably tend to keep the sails drier than they would be in its absence; and in this way it might be obnoxious to the fungi, which need moisture in order that they may thrive. So too with cordage; it might be questioned whether ropes made from hemp that has been impregnated with the oil mordant (and tannin), instead of with tar, would not be specially serviceable in some cases.

Bussey Institution (of Harvard University), *August*, 1883.

REVIEWS AND REPORTS.

Report on Analytical Chemistry.

Sulphur.—A test for hydrogen sulphide.—Emil Fischer[1] recommends for the detection of hydrogen sulphide, its reaction with para-amido-dimethyl aniline and ferric chloride, by which H. Caro showed that methylene blue is produced. In order to detect very small quantities of hydrogen sulphide in aqueous solution, it is treated with about $\frac{1}{10}$ of its volume of fuming hydrochloric acid, a few grains of sulphate of p-amido-dimethyl aniline, and, as soon as this is dissolved, a drop or two of dilute ferric chloride. If hydrogen sulphide is present the solution becomes clear blue after a short time and the color is permanent. The addition of hydrochloric acid prevents the formation of a red dye by ferric chloride and amido-dimethyl aniline which is formed in neutral or weakly acid solution. It is possible to detect, in this way, 0.000018 gram of hydrogen sulphide in a litre of water, where neither lead acetate nor sodium nitro-prussiate gives a reaction.

P-amido-dimethyl aniline may be prepared very readily from the dye "helianthine" by reduction with zinc dust and hydrochloric acid, or by ammonium sulphide.

The detection of free sulphuric acid in the presence of aluminium sulphate.—Oscar Miller[2] shows that methyl orange not only furnishes a test for free sulphuric acid in presence of aluminium sulphate, but also admits of its determination with methyl orange as indicator. 0.01 gram of free acid has been detected in 1 litre of water containing also 0.645 gram aluminium sulphate. Ethyl orange is also very sensitive towards free sulphuric acid, but is also colored rose-red by neutral aluminium sulphate.

Nitrogen.—A new method for the determination of nitrogen in organic substances has been proposed by J. Kjehldahl.[3] The method is somewhat similar in principle to that proposed by Wanklyn as a modification of his albuminoid ammonia process in water analysis. By Wanklyn's method the nitrogenous substance is oxidised by potassium permanganate in alkaline solution. In the method now proposed by Kjehldahl, the oxidation is accomplished by the same reagent, but in strongly acid solution. The substance is heated for some time with an excess of concentrated sulphuric acid, to near the boiling point; the solution thus obtained is oxidised by adding an excess of dry powdered potassium permanganate. Under these conditions the nitrogen of organic substances in general is

[1] Berichte der deutschen chemischen Gesellschaft, **16**, 2234. [2] *Ibid.*, 1991.
[3] Zeitschrift für analytische Chemie, **22**, 366.

converted into ammonium sulphate, from which the ammonia is distilled, after supersaturation with caustic soda, and determined by titration in the ordinary way. The essential conditions, under which the process admits of satisfactory results, are, that ammonium sulphate suffers no decomposition at the high temperature used, nor in the subsequent oxidation, and that the energetic phenomena which accompany the oxidation can be regulated so as to avoid loss of substance. The details of the process are simple and admit of many analyses in a day. The substance is weighed off in a small flask in which the oxidation is to be performed. The amount of sulphuric acid to be added may vary between moderate limits, but about 10 cubic centimeters are generally used. This is added to the flask and the whole heated for about two hours until all reaction has ceased. The potassium permanganate in powder is added slowly in a small but constant stream, and in a few minutes a dark green color shows the oxidation to be complete. After cooling, the liquid is diluted with water and removed to a flask holding ½ litre, where, after the addition of caustic soda, the ammonia is distilled off into an absorption bulb and estimated with standard acid. Small pieces of zinc are added to the distilling flask to prevent the violent, irregular boiling always noticed when ammonia is distilled.

For titrating the ammonia or the excess of standard acid in the absorption apparatus, any of the ordinary methods may be used, but the author recommends particularly the method based on the fact that a mixture of potassium iodate and iodide yields free iodine with an acid, which may be titrated with sodium hyposulphite and starch paste, with such sharpness as to make the method preferable to any other when ammonia is to be determined from substances containing only a very small percentage of nitrogen.

A list of analyses of various organic substances by this method indicates that it is capable of very exact results, but is not applicable to substances containing nitrogen in the form of volatile acids, as the cyanogen compounds or oxides of nitrogen. With a few alkaloids, notably quinine, the entire nitrogen is not evolved.

Determination of ammonia in plant juices and extracts.—Two methods are in use for the estimation of the ammonia in plants: either the liquid is treated with milk of lime and the ammonia taken up in titrated acid as it evaporates (Schlösing's method), or it is distilled with magnesia. E. Bosshard[1] has shown, however, that when asparagine or glutamine is present in plant extracts, the results are too high. If these amides are removed by Schulze's method of precipitating with nitrate of mercury the results are too low. But by precipitating the ammonia with phospho-tungstic acid and distilling the finely divided precipitate with magnesia, satisfactory results are obtained. The extract is acidified with hydrochloric or sulphuric acid, then treated with phospho-tungstic

[1] Zeitschrift für analytische Chemie, 22, 329.

acid in excess, and filtered after one or two hours. That part of the precipitate which adheres to the glass is dissolved off by hot water and added together with the filter to the distillation flask, magnesia added and the determination made as usual.

A new method for the estimation of minute quantities of carbon.[1] By J. E. Stead. The method depends on the fact that the carbon present in iron and steel is soluble in a solution of caustic soda, and can be determined by the depth of color which it imparts to the latter. A specimen of iron is dissolved in nitric acid and treated with caustic soda of a certain strength. The colorimetric estimation of the carbon is then effected by comparing the depth of color with that of different lengths of a standard solution. It is shown that the carbon is not oxidised when boiled with nitric acid even after the complete solution of the iron. The author recommends a special form of apparatus for the colorimetric test.

Alkalimetry.—J. Wieland[2] has made a comparative study of the various indicators for the detection of free acids and alkalies. Ethyl-orange is, according to Wieland's results, the most sensitive indicator known; and it also exceeds other indicators in the sharpness of its change in color. The following scheme represents the various indicators in the order of their delicacy. The numbers representing the sensitiveness indicate the number of cubic centimeters of hundredth normal acid or alkali necessary to cause a change of color in 50 cc. of a solution containing 2 drops of a .05 per cent. solution of the indicator.

	Change of color by titrating an alkali with an acid.	Sensitiveness toward Acids.	Alkalies.
I. Not affected by CO_2.			
Ethyl-orange,	Orange to rose color.	0.3–0.5	...
Methyl-orange,	Yellow to orange. " to rose.	0.3–0.5	...
Phenacetolin,	Brown-red to yellow-green,	0.3	0.3 Na_2CO_3
Sodium alizarinsulphonate,	With KOH, red to orange.	0.1	0.6
	With Na_2CO_3, red to yellow.		
Cochineal,	Blue-red to yellow-red.	...	0.3
Tropäolin, OO,	Yellow to orange.	Not very sensitive.	
Fluorescein,	Loses fluorescence.		
II. Affected by CO_2.			
Nitrophenol,	Yellow to colorless.	...	0.5
Phenol phthaleïn,	Blue to colorless.	...	1.5–2.0
Flavescin,	Yellow to colorless.	...	0.5–1.0
Alizarin,	Blue-red to yellow.	0.3	...
Litmus after Kretschmar,	Blue to yellow-red.	0.5	...
Pararosolic acid,	Red to yellow.	...	0.6
Eupittonic acid,	Blue to brown-red.	...	0.9
Rosolic acid (coraline),	Blue-red to red.	...	0.6

The brackets indicate those nearly the same in the sharpness of the change.

[1] Chemical News, **47**, 285. [2] Berichte der deutschen chemischen Gesellschaft, **16**, 1989.

Iron.—Zimmermann has shown that Margueritte's method for determining iron by potassium permanganate can be used in the presence of hydrochloric acid if manganese sulphate is added. It is now shown by J. Krutwig and A. Cocheteux[1] that the manganese sulphate may be omitted if precautions are taken: 1, to use as little hydrochloric acid as possible for the solution of the iron (10 cc. for .1 gram iron ore); 2, to reduce with zinc in the hydrochloric acid solution; 3, to add twice as much sulphuric acid as there is hydrochloric acid present; 4, to dilute the solution to 300 cc. and to use a dilute permanganate solution for the titration.

Petroleum.—F. Beilstein[2] has made a comparative study of the various forms of apparatus which have been proposed for determining the inflammability of petroleum by means of its flashing point. The forms of apparatus of Abel, Engler and others give concordant results under proper management, but require that the instruments be constructed exactly alike, or two instruments of the same make will give different results. Thus two specimens of Engler's apparatus apparently of the same dimensions gave a difference of 2°. The reason for this was, that the marks to which the petroleum is to be poured were not at the same level. Liebermann's method is the only one which is free from these objections. The results in this case are independent of the amount of petroleum and of the air passed through, as has been verified by Stoddard. Stoddard's apparatus consists of a cylinder 2–3 cm. wide and 10–12 cm. long, open at top and closed by a cork below, which admits a glass tube for forcing air through the petroleum which fills the cylinder to one-third its height. The cylinder is placed in a water-bath, air forced through, until a light held at the mouth ignites the vapor.

Beilstein shows that the flashing point in this apparatus varies with the width of the cylinder, and that this must always be to the height as 1 to 5 or 7. When volatile oils are present in the petroleum the result is affected by the time during which air is passed through. After studying all the conditions which affect the determination of the flashing point, the author adopts the following method as capable of most concordant results. An ordinary glass cylinder 35 mm. wide and 175 mm. high, has a mark 60 mm. from the bottom and a second at 70 mm. from the bottom. The petroleum is poured in to the lower mark. Air is passed through by a doubly bent tube which has a rose-formed end to subdivide the air bubbles. The cylinder is placed in a water-bath the temperature of which is raised slowly (one degree in two or three minutes). At each degree air is passed through for five seconds, so rapidly that the foam from the petroleum reaches the second division. At the same time a small flame is held at the mouth of the vessel. The first determination gives only approximate results. The petroleum

[1] Berichte der deutschen chemischen Gesellschaft, **16**, 1534.
[2] Zeitschrift für analytische Chemie, **22**, 309.

must be replaced by a fresh supply, the observations are then begun at the temperature obtained in the first determination. If the petroleum is not heated too rapidly so that the temperature of the bath outside the cylinder is only about one degree higher than that within, the difference between single determinations need not be greater than ½ degree.

The method of determining the safety of oil by its flashing point gives no indication of the actual value of the oil for use in lamps. Petroleum which is rich in heavy oils shows, naturally, a satisfactory flashing point, but cannot be used in ordinary lamps. Distillation is the only method by which the nature of petroleum can be determined from all points of view. In order to obtain concordant results by distillation, certain precautions are necessary, which may be best fulfilled by the following process. A round flask provided with a Glinsky's dephlegmator is weighed, then the petroleum added and weighed again. The distillates are collected in a weighed receiver after passing through a tube ¾ meter long without a condenser. The distillation is so conducted that about two grams distil in a minute. The distillate below 150° is weighed as light oil, that from 150°–270° as oil suitable for burning purposes, and the residue in the distilling flask weighed when the temperature reaches 270°. The amount of heavy oil boiling above 270° must be less than 15 per cent. of the entire oil, although this may go higher in Caucasian petroleum. If the light oil is less than five per cent. the oil may be regarded as safe.

Methyl aldehyde.—L. Legler[1] proposes a method for determining methyl aldehyde which is based upon the following reaction with ammonia:

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

The reaction takes place even with dilute solutions of ammonia, and is completed in a short time without the formation of any secondary products. The solution containing methyl aldehyde is titrated with an excess of a standard ammonia solution, and this is titrated again with normal sulphuric acid. With alkalies the reaction is:

$$2CH_2O + NaOH = HCOONa + CH_3OH,$$

which is also capable of yielding concordant results, but it is necessary to warm the solution for some time before the reaction is complete, and if the mixture is heated rapidly the results are too low.

As methyl aldehyde shows little tendency to transformation into formic acid in neutral or acid solution, it may be determined in presence of volatile acids by determining the sum of the acids and methyl aldehyde by titration with ammonia; sulphuric acid is then added, and by repeated distillation the volatile acids and methyl aldehydes obtained in the distillate, the acids are then

[1] Berichte der deutschen chemischen Gesellschaft, **16**, 1333.

titrated with normal alkali, and the difference between this result and the ammonia titration gives the methyl aldehyde. Similarly, methyl aldehyde may be estimated in presence of formic and acetic acids. The acids are first determined by titration with cold normal alkali. The methyl aldehyde is then converted into formic acid by heating with alkali, and the total amount of formic acid determined, the difference gives the amount of acetic acid.

The detection of urea in aqueous solution.—C. L. Bloxam[1] recommends acidifying the solution with hydrochloric acid, and evaporating on a crucible lid till thick white fumes are no longer evolved. The residue is dissolved in a drop or two of ammonia, and a drop of barium chloride added. By stirring with a glass rod, barium cyanurate is formed on the lines of friction made by the glass rod. A very characteristic test for the cyanuric acid consists in dissolving it in a drop or two of ammonia, and adding a drop of a weak solution of copper sulphate; on standing for a few minutes, a violet-colored crystalline precipitate separates. This seems to be cuprammonium cyanurate described by Wöhler.

D. T. D.

Relations of Crystallography to Chemistry.

Since it is now generally conceded that the description of no new chemical substance is altogether complete without a thorough crystallographic and optical examination of its crystals, it may not be amiss to present here a concise statement of the results already obtained in this field by German investigators, particularly from the study of the crystals of organic compounds. It has been thought that, by indicating the questions open for solution and the general end toward which such investigations are tending, an incentive might be offered to those not already conversant with them to undertake similar work in this country, where as yet little of the kind has been done.

All that has recently been accomplished by physicists and mineralogists to explain the hidden relation between the outward form and physical properties of crystals has done much to clearly bring out that still deeper mystery, the solution of which may well be regarded as the end and aim of theoretical mineralogy, viz. *The manner in which both the crystalline form and physical properties of substances are directly dependent upon their chemical constitution.* This is a question of which we as yet know very little, but it is the one upon which the work in chemical crystallography abroad is being directed, and it is one whose importance warrants the vast number of observations which must precede its solution.

The first important discovery to throw much light upon the relation between crystalline form and chemical constitution was that by

[1] Chemical News, **47**. 285.

Mitscherlich, in 1819, of isomorphism and polymorphism. It was found that different substances of analogous chemical composition possess very similar crystalline forms, and can even unite in forming a single crystal; but that, on the other hand, the same chemical substance sometimes exhibits two or three quite distinct forms, which might even belong to different crystal systems. It was hoped that these two laws, which had yielded such excellent results in inorganic chemistry and mineralogy, would prove still more useful when applied to organic compounds, which allowed of a much more satisfactory study of their atomic and molecular structure than the inorganic, but this hope was not realised. The careful investigation of various isomeric substances as well as those forming a series, whose members differ by CH_2, revealed some similar crystal forms, but even more that were totally unlike. Nowhere could any law or order be discovered. The arrangement of the atoms in an organic molecule is evidently very different from that of the metals, which may be substituted for one another in an isomorphous mixture.

In the year 1870 Paul Groth,[1] then in Berlin, published the results of some crystallographic investigations upon a number of benzene derivatives, which suggested an entirely different direction to be pursued in the study of the crystallography of organic compounds. The question he proposed to himself was the following: Given the crystalline form of an organic compound, what alterations does this form undergo by the substitution of certain atoms or groups for various hydrogen atoms? The study of a series of benzene derivatives, containing hydroxyl (OH), nitryl (NO_2), chlorine (Cl), bromine (Br), and methyl (CH_3), furnished Groth with at least a partial answer to this query, and suggested a working hypothesis, the establishment of which on more general grounds has directed the work in chemical crystallography in Germany during the past twelve years. It was found that the introduction of the hydroxyl or nitro groups into benzene altered the crystalline form only in a moderate degree, and that, too, always in such a way that, while *two* of the axes remained nearly the same, the relative value of only *one* axis and zone were noticeably affected. The effect of the introduction of chlorine (Cl), bromine (Br), and methyl (CH_3) is much more radical. These cause a change of the *crystal system* from one of higher to one of a lower grade of symmetry; but even here the values of the angles of one zone remain unaltered. Groth called this regular change of crystalline form through substitution "morphotropism," and spoke of the "morphotropic power" of an atom or group in reference to the substance in which it was substituted. The morphotropic power was stated to be dependent upon the four following circumstances:

[1] Monats-Berichte der Berl. Ak. d. Wiss. 1870, 247–258; Poggendorff's Annalen, **141**, 31; Neues Jahrbuch für Mineralogie, etc., 1871, 225.

1. The specific character of the substituting atom or group.
2. The chemical composition of the substance in which the substitution takes place.
3. The crystal system of the original substance.
4. The relative position of the substituting atom or group in the new molecule.

In 1874[1] appeared the results of a crystallographic study of the chlorine and bromine derivatives of naphthalene tetrachloride ($C_{10}H_8Cl_4$) and naphthalene tetrabromide ($C_{10}H_8Br_4$) by C. Hintze, this being a revision of the crystallography of Laurent's paper, "Sur la Série naphtalique," 1850.[2] He verifies the conclusions of Professor Groth in regard to morphotropism, and adds the new fact that different but nearly related atoms, such, for instance, as chlorine and bromine, when substituted in the same position in a molecule, produce very nearly the same morphotropic effects. Such atoms he calls "isomorphotropic." The introduction of chlorine or bromine atoms was found to produce less pronounced changes in the crystalline form of the substances here under consideration than upon that of benzene, thus proving Groth's second condition of morphotropic power.

Two years later[3] Dr. C. Bodewig published his crystallographic investigation of the dinitrobenzene series, the principal result of which was to verify Groth's assertion that the morphotropic power of the nitro-group (NO_2) is slight, and that it is dependent upon the relative position of the group in the molecule (4th condition).

In 1877 Professor Groth, of Strassburg, started the "Zeitschrift für Krystallographie und Mineralogie," a journal having for one of its avowed aims the collection and publication of material throwing any light upon the relation of crystalline form to chemical constitution. This end has been kept well in view, and during the past six years there have appeared in the pages of the "Zeitschrift" the results of a great number of investigations by many different workers in the field of chemical crystallography. These investigations relate partly to connected groups of organic substances and are partly disconnected observations to serve as material for future comparisons. A great variety of compounds are represented, but the results do not yet agree sufficiently to admit of important generalisation.

Up to the year 1877, when the number of organic substances which had been studied was comparatively small, all observations appeared to confirm the laws of morphotropism and isomorphotropism as they had been enunciated by Groth and Hintze. As soon, however, as the number of these observations commenced to increase rapidly, it was discovered that apparent exceptions to these laws were by no means uncommon, showing that, while an excellent beginning had been made, the real mystery to be solved

[1] Poggendorff's Annalen, Erg. Bd. **6**, 1874, 177-198.
[2] Revue scientifique et industrielle.
[3] Poggendorff's Annalen, **158**, 1876, 239-244.

lay far below the depths as yet explored. The necessity of a vast number of observations upon which to base any trustworthy generalisation is at once manifest, so that it cannot be considered strange that no universal law has yet been discovered.

Professor Arzruni[1] first pointed out that morphotropic relations are often wanting just where, from the nature of the substances, they are naturally to be most expected. He also in the same paper shows the uselessness of attempting to explain the crystallographic relations of isomeric substances (often apparently very interesting) before the derivatives of each have been carefully studied. Professor Strüver, of Rome,[2] while studying the derivatives of santonic acid ($C_{15}H_{20}O_4$), came upon a direct exception to Hintze's law of isomorphotropism, and also found that, contrary to expectation, the substances least related chemically showed the greatest crystallographic likeness, *e. g.* santonic acid and metasantonyl chloride are more closely related crystallographically, as are also metasantonic acid and santonyl chloride, than the acids are to their own chlorides.

Dr. O. Lehmann[3] has investigated the subject of physical isomerism. He divides all the chemical compounds which exhibit two or more crystallographically distinct modifications into two classes: 1. Those, *e. g.* ammonium nitrate, whose physical behavior is such as to indicate that the two modifications are composed of physical molecules containing a different number of chemical molecules he calls *polymeric;* 2. Those, *e. g.* paranitrophenol, whose physical behavior is such as to indicate that the two modifications are composed of physical molecules containing the same number of chemical molecules differently arranged he calls *metameric.*

But it is impossible to go into the details of all the more recent investigations, among which but little agreement or order would be discovered. Those specially interested in the subject are referred to the "Zeitschrift für Krystallographie," where synopses of the results published elsewhere will also be found. The gifted mineralogist who first turned crystallographic work in this direction has always maintained a lively interest in its progress, and will, without doubt, embody in his long-promised work on chemical crystallography all the results thus far obtained as well as many suggestions for future work.

In the meantime suffice it to say that a promising field of investigation is here open, offering tempting results to all those who will faithfully and intelligently cultivate it.

G. H. WILLIAMS.

[1] Zeitschrift für Krystallographie, 1, 434–452. [2] *Ibid.* 2 588–623. [3] *Ibid.* 1, 97–131.

PRINCIPLES OF THEORETICAL CHEMISTRY, WITH SPECIAL REFERENCE TO THE CONSTITUTION OF CHEMICAL COMPOUNDS. By Ira Remsen. Second Edition, Revised and Enlarged. Philadelphia: Henry C. Lea's Son & Co. 242 pp., 12mo.

In one way or another students of chemistry manage to learn a great many of the facts of the science, but in most cases their knowledge of the underlying principles is sadly defective. They talk glibly enough of atoms and molecules, of "bonds" and "double bonds," of valence and structure; but if asked some fundamental question, the character of the answer is pretty sure to reveal an unsatisfactory state of mind. This is largely due to the way in which chemistry is commonly taught. Beginners are brought face to face with the deepest subjects with which the most learned chemist can occupy himself. They are made to study certain "cut and dried" statements regarding atoms and bonds, etc., before they have formed any conception in regard to the nature of chemical action; and having once learned some definition of atoms and atomic weights, etc., having once learned to repeat Avogadro's law and the law of Dulong and Petit, they are allowed to go on their way under the fatal impression that they really know something about the subjects. The best of them, if they happen to come under good influences or if they have enough individuality, may recover from the barbarous treatment to which they have been subjected. Many never do recover from it.

The object of the book here noticed is to furnish the student with a logical statement of the connection between the fundamental facts and hypotheses of chemistry, to show how the latter are suggested by the former, and to point out the boundary line between them. It is intended for those who have some knowledge of the facts.

In the first part the methods for determining atomic and molecular weights are treated as fully as is necessary to make the subject clear. Then follow a chapter on the "Properties of the Elements as Functions of their Atomic Weights," and one on "Valence or Atomicity of Elements."

In the second division, which forms the principal part of the book, the much abused, yet important, subject of the Constitution or Structure of Chemical Compounds is taken up. The attempt has been made to show exactly how the prevailing views regarding structure have been evolved from the facts. The formulas in use for the principal compounds are discussed in such a way as to draw attention to the methods involved in constructing them. A careful study of this portion should put the student in a condition to see upon what basis the formulas in common use rest, and ought to do something towards remedying the serious and prevalent evil of writing formulas "because they are in the book."

The treatise concludes with a short chapter on the Determination of the Constitution of Chemical Compounds by Physical Methods.

THE MEDICAL STUDENT'S MANUAL OF CHEMISTRY. By R. A. Witthaus, A. M., M. D. New York: William Wood & Co. 1883.

This is a well-written book which is evidently the result of a good deal of careful thought. It is much more accurate than the books which are frequently put in the hands of medical students. In the preface occurs this passage: "In the preparation of this Manual the author has striven to produce a work which should contain as much as possible of those portions of special chemistry which are of direct interest to the medical practitioner, and at the same time to exclude so far as possible, without detriment to a proper understanding of the subject, those portions which are of purely technological interest. The descriptions of processes of manufacture are therefore made very brief, while chemical physiology and the chemistry of hygiene, therapeutics, and toxicology have been dwelt upon." There is always more or less danger in teaching elementary chemistry with reference to particular applications to be made of it. The fundamental facts and principles of the science should first be taught in the same broad way to every one beginning the study, no matter what use he may intend to put his knowledge to. In books on chemistry written avowedly for medical students, one is apt to find that principles are often lost sight of or sacrificed for the sake of describing the constituents of some ointment or wash. This kind of fault is by no means characteristic of the book under consideration. Further, the book is readable, which is more than can be said of the average chemical text-book. On the whole, if there must be books on chemistry written for medical students, it is well that there is one as satisfactory as this to recommend to them.

The most original feature in the book is the classification of the elements. They are divided into four classes, as follows:

CLASS I.—*Typical elements.*

CLASS II.—*Elements whose oxides unite with water to form acids, never to form bases. Which do not form oxysalts.*

CLASS III.—*Elements whose oxides unite with water, some to form bases, others to form acids. Which form oxysalts.*

CLASS IV.—*Elements whose oxides unite with water to form bases; never to form acids. Which form oxysalts.*

The typical elements are hydrogen and oxygen, and they are called so, "for the reason that although they differ from each other in many of their properties, they together form the basis of our classification."

Any classification of the elements into distinct families or groups must be imperfect for the reason that one and the same element may under different conditions exhibit quite different properties. In the author's scheme the analogies between oxygen and sulphur, between chromium and sulphur, between vanadium and the members of the phosphorus group, are not taken into account.

The plan of beginning a book with information in regard to the fundamental laws and conceptions of chemistry is one which is very commonly followed, but which is nevertheless surely illogical. It is certain that a beginner cannot comprehend the discussion of such matters, however clearly it may be written. For example, how is the average medical student, or any other student, to understand such statements as: "A radical, or compound radical, is a non-saturated group of atoms which behaves like an atom of an element" . . . . "thus the nitric acid molecule consists of the radical NO_2, combined with the group OH," etc, before he has acquired considerable knowledge of chemical elements and compounds, and of their conduct towards each other? Would it not be better to leave most of this out of a book intended specially for medical students? Similar exception might be taken to the free use of graphic formulas without a sufficiently full explanation of their exact significance. It is of infinitely greater value to the student at the beginning of his career to know that benzene has the composition represented by the formula C_6H_6; that it undergoes certain transformations; that it differs in certain ways from marsh gas and from ethylene, than to know that in speculating upon the nature of this substance chemists have concluded that, for good reasons, the constitution of the body may be expressed by a hexagonal shaped formula. But give the beginner the hexagon and he is apt to feel that he knows something about the compound. He can write the formula, what more can we expect of him?

This is not an imaginary difficulty. To one who comes in daily and hourly contact with students of chemistry it is something very tangible.

NOTES.

Bleaching Powder and Analogous Substances.

Kraut[1] has endeavored to show that the conclusions concerning bleaching powder to which the investigations of Odling and of Lunge and Schäppi have led, are incorrect. Odling's view is that bleaching powder consists principally of a compound $Ca<^{Cl}_{OCl}$. This view is based largely on the fact that all the chlorine can be driven out of bleaching powder by a current of dry carbon dioxide, which would not be the case if part of the chlorine existed simply as chloride of calcium. But Kraut finds that when carbon dioxide and chlorous oxide, Cl_2O, are passed together over basic chloride of calcium, the chlorine is given off, from which he concludes that

[1] Annalen der Chemie, **214**, 354.

when carbon dioxide acts on bleaching power it liberates hypochlorous acid, which, with carbon dioxide, decomposes calcium chloride. Further, he finds that a compound with bleaching properties can be made from lithium hydroxide, and the idea of a compound analogous to $Ca<^{Cl}_{OCl}$ is inadmissible with a univalent element.

In reply to these arguments, LUNGE and NAEF[1] show that when basic chloride of calcium is treated with Cl_2O alone, a certain amount of bleaching powder is formed; and on passing carbon dioxide over this, only the chlorine which was in the form of bleaching powder is driven out, the rest remaining as chloride. Further, that when chlorous oxide is passed over pure calcium chloride, some of the latter is converted into bleaching powder, thus: $CaCl_2 + ClOH = CaOCl_2 + HCl$.

This shows incidentally that the surplus of calcium hydroxide which is found in bleaching powder is not an essential feature of the compound, as has frequently been supposed; for, in the experiment above, bleaching powder is made from calcium chloride, and contains no calcium hydroxide whatever. Lunge and Naef next pass a mixture of chlorous oxide and carbon dioxide over pure calcium chloride with the object of finding whether the mixture of gases acts differently from chlorous oxide alone. They find that at first carbon dioxide serves merely to dilute the chlorous oxide and delay its action on calcium chloride. But when bleaching powder has been formed, carbon dioxide decomposes it as before.

These experiments may be explained in two ways, in so far as they concern the effect of carbon dioxide upon bleaching powder. The fact that free chlorine and not hypochlorous acid is evolved is most easily explained by supposing bleaching powder a chemical compound of calcium chloride and hypochlorite with the simple formula $Ca<^{Cl}_{OCl}$, and that carbon dioxide substitutes both the chlorine atoms, giving calcium carbonate. By the second supposition, that bleaching powder is a mechanical mixture of calcium chloride and hypochlorite, carbon dioxide must first set free hypochlorous acid, which acts on the calcium chloride portion, producing a second quantity of bleaching powder, and so on until by successive conversions into bleaching powder all the chlorine is exhausted. It would be expected in this view of the reaction that a considerable portion of the chlorine would pass out in the form of Cl_2O, when in reality it is shown by experiments on the point that it is almost entirely free chlorine. The amount of hypochlorous acid liberated is almost vanishingly small, and is due to the extra moisture present, which splits up the compound into $CaCl_2$ and $Ca(OCl)_2$, as in the case where bleaching powder is dissolved in water.

Kraut has stated that lithium hydroxide, when perfectly dry,

[1] Annalen der Chemie, **219**, 129.

does not absorb chlorine, and when moist only in the proportion of 2 atoms of chlorine to 4 molecules of LiOH, and that the resulting compound is analogous to bleaching powder. From these statements he argues that a certain amount of hydroxide is essential to compounds like bleaching powder, and that the explanation of Odling fails for a monad element. Lunge and Naef now show that the absorption of chlorine by lithium hydroxide may exceed very considerably the proportion of 2 atoms of chlorine to 4 molecules of LiOH, and that the resulting compound is not analogous to bleaching powder, particularly as it is only decomposed to a slight extent by carbon dioxide, unless the temperature is raised to a point where the compound begins to decompose partly into lithium chloride and oxygen and partly into chloride and chlorate; and even in this case decomposition by carbon dioxide is very small. A considerable proportion of the chlorine goes off as hypochlorous acid. When the lithium compound is allowed to stand in an atmosphere of chlorine for some time it loses a large portion of the hypochlorite, a fact which is only true to a very limited extent with bleaching powder.

Finally, Lunge and Naef investigate the action of chlorine on barium and strontium hydroxides. With the former they are unable to obtain more than traces of a bleaching compound, but its reactions are like that formed from calcium hydroxide. With strontium, however, they form a compound which is decomposed by carbon dioxide even when cold, with liberation of free chlorine, showing that the bivalent elements tend to form compounds much more analogous to bleaching powder than the compound of lithium.

D. T. D.

Note on Boron.

H. Sainte Claire Deville and Wöhler described under the name of crystallised boron some products which they obtained by reducing boric acid at an elevated temperature with aluminium. These products differed, however, in their composition as well as in their external appearance. The substance they obtained most frequently consisted of regular octahedrons of a yellow or brownish red color. The great brilliancy of the crystals, their refractive power, and their hardness resembled the diamond. They contained, however, variable proportions of carbon and aluminium. These crystals were always accompanied by a black substance having a brilliant lustre, sometimes occurring in the form of large plates or scales, transparent only in the thinnest slices. An analysis showed that they contained 2.4 per cent of carbon.

M. Hampe,[1] having studied the crystallised products known as adamantine boron, arrived at very different results from those of H. Deville and Wöhler. This chemist found that the black crys-

[1] Annalen der Chemie, **183**, 75.

talline plates do not contain carbon, that their composition may be represented by the formula AlB_6, and that they contain 17 per cent. of aluminium. They can only be obtained by reducing boric acid with aluminium in crucibles of refractory clay at the temperature of melting iron. He found the crystals to dissolve in boiling nitric acid, and their density was 2.5345 at 17.2°. The yellow or brown octahedrons, he states, contain normally 3.8 per cent. of carbon and 13 per cent. of aluminium. Hampe regards the percentage of aluminium too high to permit of the supposition that this element is an impurity. He represents the composition of the crystals by the formula $C_2Al_3B_{24}$. They are formed when boric acid is reduced by aluminium, in crucibles of carbon or graphite at a higher temperature than that at which the black crystals are formed.

There is thus a disagreement in the statements of H. Deville and Wöhler and those of Hampe. The former regarded the yellow crystals as consisting of boron with variable proportions of carbon and aluminium, the latter regards them as a definite compound. The former thought the black crystals were the same as the yellow, only impure by their large percentage of carbon. Hampe states that the black crystals contain no carbon, but are composed of boron and aluminium only.

A. Joly has undertaken to clear up the subject. He states that at the elevated temperature at which Deville and Wöhler worked only very small quantities of the large black crystalline plates were obtained. He finds that they are rarely formed when the temperature is at its maximum, but much smaller black crystals, united to the yellow ones, are formed if a small quantity of material is taken and the heating continued for a longer time. It is this substance which Deville and Wöhler probably analysed, while Hampe reduced boric acid in clay crucibles at a much lower temperature and obtained large black crystals which did not contain carbon. Joly also finds that the yellow crystals, AlB_6, dissolve readily in boiling nitric acid without leaving a sensible residue, but if the brown or black crystals obtained at a higher temperature are treated with this reagent, they are only partially dissolved, a carbonaceous residue remaining.

The reduction products of boric acid by aluminium are therefore as follows:

1st. The boride AlB, occurring in yellow hexagonal plates, studied by H. Deville and Wöhler.

2d. The boride AlB_6, occurring as large black crystalline scales.

3d. Yellow cubical crystals, containing carbon and aluminium.

4th. A carburet of boron, or probably several carburetted products, produced, in the presence of carbon and an excess of boric acid, at an elevated temperature by the transformation of the preceding products.—(*Comptes Rendus*, **97**, 456.)

E. H. K.

Samarium and its Compounds.

This element was discovered by Lecoq de Boisbaudran in samarskite about 1878. Since then considerable doubt has existed in regard to its nature, and for a time it was thought to be identical with the decipium of Delafontaine. The properties of the element have now been carefully studied, and its atomic weight determined by P. T. CLEVE. The raw material used for extracting the oxide of samarium consisted of a mixture of almost all the rare oxides of the earth metals derived from orthite found at Arendal in Norway. The mixture of earths was treated with nitric acid and heated until it began to give off red vapors. After cooling, the mass was treated with water, which left undissolved a large quantity of basic nitrates, principally of cerium and thorium. After washing, the basic salts were mixed with strong sulphuric acid, and the solution of the sulphates in cold water was precipitated with large quantities of hot water, by which operation most of the cerium was separated as basic sulphate.

The solution was then precipitated with caustic soda, and the hydrate, principally of thorium, dissolved in dilute sulphuric acid. On evaporating, large bulky masses of thorium sulphate were obtained. The oxides which remained in the mother liquors were transformed into nitrates and added to the solution of nitrates obtained by the first operation. These nitrates were evaporated and the residue heated until red vapors were given off. On treating with water, a solution free from cerium and thorium was obtained.

The solutions free from the oxides of cerium and thorium, or containing only small traces of these oxides, were precipitated with potassium sulphate with the view of separating the cerium and yttrium oxides, of which the former were (incompletely) precipitated and the latter (incompletely) retained in solution.

The yttria earths (about 700 grams) were transformed into nitrates and subjected to the usual melting process, for the separation of erbia, from yttria, terbia and didymia. The basic nitrates thus obtained contained also a very small quantity of thulium, some erbia and ytterbia, and a considerable portion of holmia. The fractions containing yttria and didymia were saturated with potassium sulphate, and this precipitate was added to the similar precipitate formerly obtained. These difficultly soluble double sulphates were decomposed with boiling potash-ley, and the hydrates dissolved in diluted sulphuric acid were again treated with potassium sulphate. The precipitate was converted into nitrate and evaporated. The residue was heated to partial decomposition in order to separate the last remaining traces of thorium and cerium.

The soluble nitrates thus obtained, which contained principally didymium and lanthanum, but also samarium, terbium, yttrium, etc., were mixed with impure didymium, and then subjected to partial precipitation with cold dilute ammonia. The last fractions

contained much lanthanum, which was separated partly by the Mosander method and partly by precipitation with ammonia. The first precipitations were treated with dilute ammonia. In this way several fractions were obtained, containing both terbia and didymia (samarium, etc.) They were again treated several times with sulphate of potassium.

The slightly soluble double sulphates were now decomposed, and the solution of the hydrates in nitric acid was repeatedly precipitated with ammonia. Six fractions were obtained; one of these consisted of about 67 grams of light-colored oxides, which gave the spectrum of samarium, and also that of didymium. This was treated with dilute ammonia until the spectrum of didymium was completely eliminated.

The pure oxide Sm_2O_3 was converted into sulphate, and as a mean of six closely agreeing experiments the atomic weight was found to be 150.021, or in round numbers 150. In the calculation the composition of the oxide is assumed to be Sm_2O_3. As to its position in the system of Mendelejeff, the author thinks it may most probably be placed in the 8th group on the 8th line where there is a gap for a group of unknown elements.

The salts of samarium are distinguished by a peculiar spectrum composed of several bands, four of which in the blue part of the spectrum are most characteristic.

Besides the oxide, the following compounds were prepared and analysed:

Chloride of samarium, $SmCl_3 + 6H_2O$.
Chloroplatinate of samarium, $SmCl_3$, $PtCl_4 + 10\frac{1}{2}H_2O$.
Platinocyanate of samarium, $2Sm(CN)_3 + 3Pt(CN)_2 + 18H_2O$.
Nitrate of samarium, $Sm(NO_3)_3 + 6H_2O$.
Acetate of samarium, $Sm(C_2H_3O_2)_3 + 4H_2O$.
Sulphate of samarium, $Sm_2(SO_4)_3 + 8H_2O$.
Selenate of samarium, $Sm_2(SeO_4)_3 + 8H_2O$.
Oxalate of samarium, $Sm_2(C_2O_4)_3 + 10H_2O$.

The salts of samarium agree closely in composition with the didymium salts, and of all elements samarium is most nearly related to didymium, less closely to the yttria metals, the platinocyanates of the latter being wholly different from the samarium salt, which resembles the corresponding salts of cerium, lanthanum and didymium.—(*Journal of the (London) Chemical Society*, 1883, 362.)

E. H. K.